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§ 1. QUALITATIVE DISCUSSION

1.1. *Introduction*

SUPERCONDUCTIVITY has, for many years, been one of the central unsolved problems of physics. The phenomenon was discovered by Kamerlingh Onnes as long ago as 1911; many metals and alloys, below a critical temperature T_0 characteristic of the substance, have no measurable electrical resistance. At a given temperature T, below T_0, there is a threshold magnetic field $H_c(T)$, such that if $H > H_c$ the superconducting property is destroyed. The third fundamental property, discovered by Meissner and Ochsenfeld in 1933, is that a macroscopic superconductor is perfectly diamagnetic, i.e. no magnetic field can exist inside the superconductor.

A very successful phenomenological theory was advanced by F. and H. London in 1935†, but until 1950 the nature of the phenomenon remained a complete enigma. All other macroscopic properties of metals are, at least qualitatively, understood; in particular developments of Bloch's (1928) theory of metallic conduction account for the electronic properties quite well. Nevertheless, the interaction responsible for superconductivity remained obscure. Most theoretical speculations assumed a mechanism depending on some of the factors left out of the Bloch scheme, e.g. Coulomb interactions or the details of the Brillouin zone structure.

An important advance was made by Fröhlich (1950), who suggested that Bloch's electron–lattice interaction should be responsible for superconductivity. Bloch had calculated matrix elements for emission and absorption of lattice quanta by the electrons in a metal and showed that (real) processes of this kind are responsible for the normal resistance of metals. Fröhlich pointed out that Bloch's theory can be expressed as a field theory, and that it implies the possibility of virtual absorption and emission processes. These lead to an electron–electron interaction. As a consequence of this suggestion, the energy difference between the normal and superconducting states is proportional to M^{-1}, the inverse isotopic mass of the lattice ions. Soon after the prediction, the isotope effect was found experimentally, and confirms the above dependence. It is therefore quite clear that the electron–lattice interaction of Bloch is of basic importance for the understanding of superconductivity. Nevertheless, subsequent developments have been slow, on account of the great mathematical difficulties encountered (Bardeen 1950, 1951, Fröhlich 1952, 1954, Bardeen and Pines 1955). With the very recent work of Bardeen *et al.* (1957), Bogoliubov (1958 a) and Valatin (1958), however, it has been shown that the lattice–electron interaction leads to a 'condensation', and an energy gap in the excitation spectrum. The thermal properties of superconductors are accounted for quite well, and also the existence of curl-free persistent currents. But there is, as yet, no satisfactory theory of the Meissner effect (nor of the anomalous Knight shift).

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† A parameter λ with the dimensions of a length is introduced, a 'penetration depth', and the current is split into two parts, a 'normal' component $\mathbf{j}_n$ and a 'superconducting' component $\mathbf{j}_s$. The superconducting current $\mathbf{j}_s$ obeys the following equations in place of Ohm's law :

$$\left.\begin{aligned}(-4\pi\lambda^2/c)\operatorname{curl}\mathbf{j}_s &= \mathbf{B},\\ (4\pi\lambda^2/c^2)\frac{\partial \mathbf{j}_s}{\partial t} &= \mathbf{E}.\end{aligned}\right\} \qquad (1.1)$$

Before discussing the successes and limitations of the theory in its present form, it is useful to bear in mind the following properties of superconductors:

(*a*) the phenomenological theory of the Londons governs the electrodynamic properties quite well†.

(*b*) the superconducting state is a distinct thermodynamic phase, and thermodynamic formulae of the usual type can be applied to the normal-superconducting transition, in agreement with experiment.

(*c*) the actual energy difference between the normal and superconducting phases is exceedingly small ($\sim 4 \times 10^3$ erg cm^{-3}) compared with the electronic kinetic energy ($\sim 10^{11}$ erg cm^{-3}). Despite the smallness of the energy difference, many of the macroscopic properties are quite drastically altered. Apart from the electrodynamic properties, there are large anomalies in, for example, the specific heat and thermal conductivity. It is the smallness of this transition energy, compared with other relevant energies, that is responsible for many of the difficulties in constructing a theory.

Experimental evidence is rapidly accumulating in favour of an 'energy gap', i.e. there appears to be a finite separation between the ground state and all single-particle excitations. As a phenomenological model (Ginsburg 1946, Koppe 1947, 1950, Goodman 1953) the energy-gap can account for the specific heat and thermal conductivity, and for the absorption edges found in acoustic and electromagnetic absorption experiments. Further experimental evidence for an energy gap is afforded by nuclear spin–lattice relaxation time measurements.

It has been claimed (Bardeen 1956) that the energy gap model, with certain additional assumptions, shows also the correct electrodynamical properties (leading to Pippard's generalization of the London equations), but this claim has been shown not to be valid (Buckingham 1957).

The scope of this article will be restricted to an account of the development and present state of the microscopic theory. No attempt will be made to describe the phenomenological developments, nor the extent to which the phenomenological theories account for the experimental results.

1.2. *The Lattice–electron Interaction*

Bloch's (1928) theory of metallic conduction assumes that the valence electrons in a metal are nearly independent, and move in the field of the metallic ions. The Coulomb electron–electron forces are neglected or at best treated by a self-consistent field approximation (though the application of plasma theory (Bohm and Pines 1953, Pines 1953, Bardeen and Pines 1955) helps to justify this approach). In a perfectly periodic field, the single-electron wave functions are of the form

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† Detailed quantitative discrepancies exist however. To overcome them we need an improved phenomenological theory. Several have been advanced, by Schafroth and Blatt (1955, 1956), Ginsburg and Landau (1950) and Pippard (1953), the latter being probably the most successful. They all introduce an additional parameter, a 'range of order' or 'correlation length'. Qualitatively, the spatial extension of the Cooper (1956) quasi-molecules (§ 3.2) probably provides the theoretical basis for the correlation length. This aspect of the theory is, however, still insufficiently developed.

$$\psi(\mathbf{x})=\exp(i\mathbf{k}\,.\,\mathbf{x})u(\mathbf{x}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.2)$$

where $u(\mathbf{x})$ is a function with the periodicity of the lattice. The total wave function is a Slater determinant, built out of these one-electron functions. The electrons behave rather like free electrons, but with an effective mass m which may differ from the real mass.

These 'quasi-free' electrons are scattered by departures from periodicity: (*a*) lattice defects of many kinds (impurities, dislocations, vacancies, etc.) produce an approximately temperature-independent scattering—the 'residual' resistance, and (*b*) the thermal motion of the ions leads to a temperature-dependent scattering, the 'ideal' resistance, which vanishes as $T\to 0$. The latter mechanism was described by Bloch in terms of the emission or absorption by an electron of a 'phonon', a quantum of excitation of one of the normal modes of vibration of the lattice.

The realization that the interaction of lattice vibrations with electrons implies an interaction between electrons was the first essential step, made by Fröhlich in 1950. Previously Fröhlich *et al.* (1950) had studied the behaviour of an electron in an ionic medium ('polaron'). They formulated the interaction in a field-theoretical way—the electron produces a field of polarization of the lattice, and that field in turn reacts back on the electron, and leads to a self-energy. Provided the interaction is weak enough, the self-energy can be calculated by perturbation theory. The Hamiltonian for the polaron is quite similar in form to the Hamiltonian implied by Bloch's theory, except in so far as there are many electrons instead of a single one. Fröhlich, therefore, by writing the Bloch interaction in Hamiltonian form, showed that it would also lead to an electron self-energy and an electron–electron interaction†. The latter effect arises from processes in which *one* electron emits a phonon, which *another* electron absorbs.

In the Bloch model of a metal, the self-energy is by far the larger effect, but it is also the less interesting. It arises from the fact that for most lattice waves the electronic motion can follow the lattice nearly adiabatically (Huang 1951, Fröhlich 1952). The electrons enhance the inertial properties of the lattice, leading to a renormalization of the velocity of sound, and the single-particle energy levels suffer a self-energy correction. For electrons near the Fermi surface, however, another possibility exists—the lattice displacements can follow the electron density fluctuations adiabatically instead and, by reacting back on the electrons, produce an interaction between electrons.

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† Although the analogy is incomplete, a comparison with quantum electrodynamics is illuminating. There the electron–photon interaction leads to charge and mass renormalization, and to the Coulomb interaction between electrons.

One of the great difficulties confronting the development of the theory was the problem of isolating the small interaction energy, in the presence of the much larger self-energy. Application of second order perturbation theory (Fröhlich 1950) indicates the presence of the two effects, but implies that if the interaction is strong enough to be of interest, then the lattice is unstable (Wentzel 1951).

In order to isolate the (small) interaction energy and study its properties, the (large) self-energy must somehow be removed. Fröhlich (1952) showed how this can be done by a unitary transformation of the Hamiltonian. The transformation leads to (*a*) a renormalized sound velocity s (from the inertia of the electrons which follow the lattice motion), (*b*) a renormalized coupling constant, (*c*) a renormalization of single particle energy levels, (*d*) an electron–phonon interaction restricted to transitions on an energy shell, and (*e*) an electron–electron interaction energy, positive when the electron energy difference $\gtrsim \hbar k_0 s$, negative for energy differences $\lesssim \hbar k_0 s$. The order of magnitude of this energy is $\sim F\zeta_0/N_e\Omega \sim F/\Omega\Xi$ where Ω is the normalization volume, N_e the number of electrons per unit volume, F is defined in § 2.2, and is a dimensionless measure of the strength of the lattice–electron interaction, and Ξ is the density of levels, per unit volume, at the Fermi surface ζ_0.

If any 'condensation' in momentum space is to occur, it has to do so despite an increase in the electronic kinetic energy, and will therefore be restricted to an energy shell, of thickness $\sim \hbar k_0 s$ at the Fermi surface. This shell will contain $\sim \hbar k_0 s \,.\, \Omega\Xi$ electrons, and therefore the interaction energy will be roughly

$$\frac{F}{\Omega\Xi}\{\hbar k_0 s\Omega\Xi\}^2 \sim Fms^2N_e\Omega$$
$$\sim FN_e\Omega(m/M)\chi, \qquad (1.3)$$

where χ is independent of the isotopic mass M of the ions. The dynamic nature of the effect is apparent in the dependence of the energy on the isotopic mass, via the sound velocity s.

The condensation energy is proportional to the square of the threshold field at absolute zero, and hence the theory predicts

$$H_c(T=0) \propto M^{-1/2}. \qquad (1.4)$$

Since empirically $H_c(T=0) \propto T_0$, the prediction can also be written

$$T_0 \propto M^{-1/2}. \qquad (1.5)$$

Both these predictions (1.4) and (1.5) are in quantitative agreement with experiment (Maxwell 1950, Reynolds *et al.* 1951, Allen *et al.* 1950 a, b, Lock *et al.* 1951). These experiments indeed afford the most direct evidence that the electron–phonon interaction is responsible for superconductivity. The condensation energy (1.3) is however too large, compared with observed values, by a factor $\sim 10^2$. Since $\hbar k_0 s \sim \kappa\Theta$, where κ is Boltzmann's constant and Θ is the Debye temperature, (1.3) would predict $T_0 \sim \Theta$, while usually the values satisfy $10^{-2}\Theta < T_0 < 10^{-1}\Theta$.

The low-lying excitations of a metal are highly degenerate; consequently it is not satisfactory to use the Bloch wave functions as unperturbed states in a perturbation theoretical approach. The perturbation theoretical calculation of Fröhlich (1950) served mainly to bring out the above orders of magnitude, and to predict the isotope effect†.

For a system with an n-fold degenerate level, where n is finite, there is a well-known systematic procedure for selecting appropriate linear combinations of the degenerate wave functions, to lift the degeneracy. But for a continuum, there is no such systematic procedure. For further progress, clearly, what is needed is a new set of 'unperturbed' wave functions, formed by appropriate linear combinations of Bloch functions. In 1953, Casimir commented: "...I believe that one should try to make a good guess as to what the state of affairs is, and then calculate the energy." Further progress indeed awaited the 'good guess'.

One of the features which is lacking in the Bloch wave functions and which the improved basic functions should exhibit is the cooperative nature of the phenomenon. The specific heat at $T = T_0$ shows a discontinuity, an Ehrenfest (1933) "transition of second order". Just as the Weiss (1907) theory of ferromagnetism assumes an 'internal field', which acts as an order parameter and vanishes at the Curie temperature, so we can demand a parameter here with a similar role. It is also desirable that the order parameter should have an obvious physical significance (as the Weiss field certainly has), so as to give as much insight as possible into the behaviour of the system.

Up to about 1954, the *sole* success of the theory had been to predict the isotope effect, while in all other directions it had encountered such severe mathematical difficulties that it was doubtful whether the mechanism could produce a condensation. It was therefore desirable to show that a condensation of some sort *could* occur as a result of the electron–phonon interaction, even in a simplified model, with unrealistic values of the parameter. Fröhlich (1954) studied a one-dimensional model with very strong coupling. In a one-dimensional metal the degeneracy is much lower than in three dimensions. By making the interaction sufficiently strong, he was able to neglect the recoil of the lattice modes when an electron is scattered, and to develop a Hartree self-consistent field approximation. The lattice mode of wave number $w_0 = 2k_0$ can become strongly excited, and acts as a spatially periodic field on the electrons, producing a gap in the single-particle energy spectrum (Peierls 1930). The electron density varies with the same periodicity, producing the periodic lattice distortion in a self-consistent way (§ 3.1). The approximations are valid only if the coupling is very strong (which implies $T_0 \gg \Theta$).

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† Starting from a knowledge of the experimental discovery of the isotope effect, Bardeen (1950) developed another formulation, which he later showed (1951) to be equivalent to Fröhlich's.

The resulting energy gap is

$$\Gamma = \zeta_0 \exp(-3/2F), \qquad (1.6)$$

and the condensation energy per atom

$$W = \zeta_0 \exp(-3/F) \qquad (1.7)$$

where $\zeta_0 = \hbar^2 k_0^2/2m$ is the Fermi energy. The isotope effect has been lost, because the dynamic properties of the interaction have been ignored. The excitation of the lattice mode $w_0 = 2k_0$ acts as an internal field, whose quantum properties have been neglected. This single mode is so strongly excited that the electronic motion follows it adiabatically; this is just the condition we need in order that the interaction energy is as large as possible compared to the self-energy. In fact these two energies come out of the same order of magnitude.

The amplitude of the lattice mode acts as an 'internal field', and provides the sought-after analogy with ferromagnetism at absolute zero. Moreover the self-consistent calculation can be extended to finite temperatures, giving a temperature-dependent gap width $\Gamma(T)$ which vanishes at some temperature T_0, again in analogy with the Weiss field. The specific heat is exponential near $T = 0$, and has a discontinuity at T_0 (Kuper 1955).

Although the 'Hartree field' method cannot be generalized, either to three dimensions or to weaker interactions, it is important in giving an energy gap proportional to $\exp(-3/2F)$. This function has an essential singularity at $F = 0$, and cannot arise in *any* finite order perturbation theory. If for some reason the exponential factor should prove to be correct, even in a three-dimensional system with weak coupling, then one can understand the smallness of the condensation energy of the superconducting phase compared with (1.3), since $\exp(-1/F)$ is a very rapid function of F, and, for example, is $\sim 10^{-2}$ for $F \sim 1/5$. Also since F will vary a little under compression, the very sensitive observed pressure dependence of T_0 would follow.

The reason the one-dimensional model shows no isotope effect is that the interaction has been made so strong that *all* electrons follow the lattice motion adiabatically—the lattice motion is treated quasi-statically. If we can restore the dynamic properties of the interaction, we might hope to get an energy containing both the factor ms^2 of the perturbation method and the exponential factor of the Hartree field method.

By the choice of a good set of trial wave functions, Bardeen *et al.* (1957) achieve just this desired combination. Cooper (1956) had noticed that under the superconductive interaction, two electrons near the Fermi surface could form a 'molecule'. If indeed *all* (or at least *many*) of the electrons could become bound in pairs, and if these pairs did not overlap appreciably, then, as Schafroth *et al.* (1957) had shown, the system would exhibit superconducting properties by virtue of the Bose–Einstein condensation of the (Boson) 'molecules', the condensed phase being made up of pairs with zero total momentum. Actual Cooper pairs are not highly localized; the spread is $\sim 10^{-4}$ cm, so that the appearance of the condensed phase does not arise in quite this simple way. The essential features are still present in the Bardeen–Cooper–Schrieffer ground state wave function; electrons are all correlated in pairs, with equal and opposite momenta.

As in the one-dimensional model, the spectrum of elementary excitation energies has a gap. There are also collective motions of the whole electronic system, with low energies; these have a macroscopic non-zero current (again as in the one-dimensional model). The superconducting ground state is energetically more favourable than the Bloch ground state *for all positive F, however small.* Bardeen, Cooper and Schrieffer however take the screened Coulomb interaction into account in an approximate way; the Coulomb repulsion makes a negative contribution $-A$ to the 'effective' coupling constant, $F-A$, say, and the criterion for superconductivity is that the 'effective' coupling constant $F-A$ is positive.

The condensation energy found by Bardeen, Cooper and Schrieffer is (neglecting the Coulomb repulsion)

$$W \simeq ms^2 \exp(-2/F), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.8)$$

and should be compared with (1.7) and (1.3). The desired linking of the exponential factor with the isotope effect factor ms^2 has been achieved.

The derivation of (1.8) by Bardeen, Cooper and Schrieffer requires many simplifications and approximations; in particular the lattice has only one vibrational frequency, and the matrix elements of the (renormalized) Hamiltonian are replaced by a simplified set. In consequence, the results require justification in a more rigorous fashion. A transformation of the Hamiltonian, proposed by Bogoliubov (1958 a, b) and Valatin (1958) provides the necessary justification. This transformation is an extension to a system of Fermions of Bogoliubov's (1947) Boson transformation. It introduces a new set of field variables to replace the original electron field. The transformation exhibits, in a fairly explicit form, the $(+\mathbf{k}, \uparrow\ ;\ -\mathbf{k}, \downarrow)$ electron pair correlations in the ground state. The new variables can be thought of as describing a set of 'quasi-particles'. Although the number of real electrons is a constant of the motion, the number of quasi-particles unfortunately is not†. By a suitable choice of the parameters of the transformation, the 'vacuum' state with no quasi-particles becomes identical with the ground state of Bardeen, Cooper and Schrieffer. A simultaneous transformation of the phonon field variables exhibits Fröhlich's renormalization (up to second order in the coupling constant). The energy spectrum of excited states, calculated from the transformed Hamiltonian, exhibits an energy gap

$$\Gamma \sim \hbar k_0 s \exp(-1/F) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.9)$$

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† The non-conservation of quasi-particles is linked with the difficulty in getting a clear physical picture of the mechanism of the 'internal field', in contrast to Fröhlich's one-dimensional case, § 3.1.

at absolute zero. (It is interesting to compare (1.8) and (1.9) with (1.6) and (1.7)—see § 3.2.)

At higher temperatures, a self-consistent calculation shows, as in the one-dimensional case, that the gap $\Gamma(T)$ diminishes with increasing temperature T, vanishing at some temperature T_0. The second-order transition and all other properties which depend mainly on the energy gap and the density of states follow immediately, in good agreement with experiment. Examples are the specific heat (Zavaritskiĭ 1957, Lynton *et al.* 1957, Corak *et al.* 1954, Corak and Satterthwaite, 1956), thermal conductivity (Goodman 1953, Laredo 1955, Montgomery 1957), acoustic absorption (Morse and Bohm 1957), electromagnetic absorption (Glover and Tinkham 1956, 1957, Biondi *et al.* 1958, Richards and Tinkham 1958), and spin relaxation time (Hebel and Slichter 1957).

For these problems, the size of the energy gap acts as the 'order parameter' or 'internal field'. To this extent there is a parallelism between superconductivity and other cooperative phenomena like ferromagnetism. The electrodynamical properties of superconductors are less well understood. The mere existence of an energy gap at the Fermi surface does not of itself imply superconductivity—it is equally characteristic of insulators. The vanishing of resistance is, perhaps, plausible, since collective states of motion exist in which the electron system, *as a whole*, has a non-zero momentum. These states can have energy as close as we wish to the ground state, since they are states of a system of macroscopic mass. These curl-free current distributions may be metastable, since no single-particle transition will be able to destroy the current.

The derivation of the Meissner effect—i.e. the totally diamagnetic property, or the first of the London equations (1.1), is more difficult. Without a direct physical picture of the significance of the 'internal field' parameter, one cannot hope to get much insight into how the magnetic field is excluded from a body, and hence no guidance in making useful approximations. In this situation it may be dangerous to make any approximation at all; Schafroth (1951, 1958) has shown that unless the derivation is strictly gauge-invariant, the predicted Meissner effect can be modified *arbitrarily* by a suitable gauge transformation.

§ 2. The Hamiltonian Formulation

2.1. *Outline of the Bloch Theory*

In Bloch's (1928) theory of conduction in metals, the electron–electron interactions are neglected, and the lattice is regarded, in the first instance, as providing only a static spatially periodic field†. The time dependent

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† Since the electron density will also have the periodicity of the lattice, a Hartree self-consistent treatment of the electron–electron interactions is (Bardeen 1937), in principle, possible within the framework of the Bloch theory. The effect of electronic correlations cannot be handled thus, however, but have to be treated by, for example, the Bohm–Pines plasma theory (Bohm and Pines 1953).

Schrödinger equation for the entire electron system separates into single-particle Schrödinger equations

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}(\mathbf{r}_i)+V(\mathbf{r}_i)\psi_{\mathbf{k}}(\mathbf{r}_i)=E_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}_i) \quad . \quad . \quad . \quad (2.1)$$

where $\mathbf{r}_i$ is the coordinate of the ith electron, $\psi_{\mathbf{k}}$ and $E_{\mathbf{k}}$ are an eigenstate and the corresponding energy eigenvalue. Periodic boundary conditions will be assumed, in a box of volume Ω, containing an integral number $N\Omega$ of lattice cells. The Pauli exclusion principle is satisfied by writing, for the total wave function, a Slater determinant,

$$\Psi=\det\psi_{\mathbf{k}}(\mathbf{r}_i). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.2)$$

In (2.1), $V(\mathbf{r})$ has the periodicity of the lattice, i.e.

$$V(\mathbf{r})=V(\mathbf{r}+n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

where n_1, n_2, n_3 are integers, and $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are the basic lattice vectors. Using the periodicity of V, it is easily shown that the solution $\psi_{\mathbf{k}}$ have the form

$$\psi_{\mathbf{k}}(\mathbf{r})=\exp(i\mathbf{k}\,.\,\mathbf{r})\,u_{\mathbf{k}}(\mathbf{r}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.4)$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice, and where the components of $\mathbf{k}$ are integer multiples of $(2\pi/\Omega)^{1/3}$. Sufficiently close to an atomic nucleus, $u_{\mathbf{k}}(\mathbf{r})$ is, of course, asymptotically the wave function of an electron in a free atom.

In the absence of any lattice irregularity, these solutions (2.4) are exact eigenstates, and the electrons suffer no scattering. The 'residual' resistance of metals arises from scattering of Bloch electrons by static lattice imperfections, and will not be of interest here. The 'ideal' resistance, in contrast, is a dynamic effect, arising from the thermal motion of the ions.

If the displacement field of the ions from their equilibrium positions is denoted $\mathbf{P}(\mathbf{r})$, the change in potential of an electron at a point $\mathbf{r}$ will be approximately

$$V_1=-\mathbf{P}\,.\,\nabla V(\mathbf{r})\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.5)$$

the model has been implicitly extended to include an interaction between the electrons and the longitudinal displacement field of the lattice. The lattice displacement field in isolation may, in the usual way, be resolved into a set of harmonic oscillators. The interaction will then lead to transitions, in which a 'phonon' (a quantum of excitation of a single normal mode of the lattice) is absorbed or emitted by an electron. In these transitions, the total wave number is conserved, apart from integer multiples of the basic vectors of the reciprocal lattice†.

The matrix elements for transitions from a state with $n_{\mathbf{w}}$ phonons to one with $n_{\mathbf{w}}\pm 1$ phonons are

$$\left.\begin{aligned}(\mathbf{k},n_{\mathbf{w}}\,|\,V_1\,|\,\mathbf{k}+\mathbf{w},n_{\mathbf{w}}-1)&=\tfrac{2}{3}C\{\hbar\omega_{\mathbf{w}}/N\Omega M s_0{}^2\}^{1/2}\,n_{\mathbf{w}}{}^{1/2},\\(\mathbf{k},n_{\mathbf{w}}\,|\,V_1\,|\,\mathbf{k}-\mathbf{w},n_{\mathbf{w}}+1)&=\tfrac{2}{3}C\{\hbar\omega_{\mathbf{w}}/N\Omega M s_0{}^2\}^{1/2}(n_{\mathbf{w}}+1)^{1/2}\end{aligned}\right\} \quad (2.6)$$

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† Transitions in which this vector in the reciprocal lattice is different from zero are known as " umklappprozesse " (Peierls 1932).

(see, e.g., Sommerfeld and Bethe 1933), where N is the number of atoms per unit volume, M the mass of an ion, s_0 the sound velocity of the ion system and

$$C=3\int_{\text{lattice cell}} \frac{\hbar^2}{2m}\,|\operatorname{grad} u_{\mathbf{k}}(\mathbf{r})|^2\,\mathrm{d}^3r. \qquad (2.7)$$

C is only slightly dependent on **k** and will be treated as a constant energy: it is of the same order of magnitude as the Fermi energy ζ_0.

2.2. *The Quasi-Free Electron Model*

In Bloch's theory, although the transition matrix elements are calculated, no explicit Hamiltonian is ever written down. Fröhlich (1952) showed that it is advantageous to rewrite the Bloch theory in Hamiltonian form; it is a field theory, in which the role of 'virtual' transitions may be investigated by field-theoretical techniques, such as, for example, unitary transformations.

Bloch's matrix elements (2.6) follow from the Hamiltonian

$$H=H_{\text{el}}+H_{\text{phon}}+H_{\text{int}}+H_{\text{Coulomb}}, \qquad (2.8)$$

where the energy of the electrons is

$$H_{\text{el}}=\sum_{\mathbf{k},\sigma}\epsilon_k a^+_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma}, \qquad (2.9)$$

ϵ_k is the energy of a single Bloch electron of wave number **k**, $a^+_{\mathbf{k}\sigma}$, $a_{\mathbf{k}\sigma}$ are canonical creation and destruction operators for an electron of wave number **k**, spin σ, and satisfy the anti-commutation rules

$$\left.\begin{aligned}[a_{\mathbf{k}\sigma}{}^+, a_{\mathbf{k}'\sigma'}{}^+]_+=[a_{\mathbf{k}\sigma}, a_{\mathbf{k}'\sigma'}]_+=0,\\ [a_{\mathbf{k}\sigma}, a_{\mathbf{k}'\sigma'}{}^+]_+=\delta_{\mathbf{k}\mathbf{k}'}\,\delta_{\sigma\sigma'}.\end{aligned}\right\} \qquad (2.10)$$

It is convenient to define

$$f_{\mathbf{k}\sigma}=a_{\mathbf{k}\sigma}{}^+a_{\mathbf{k}\sigma} \qquad (2.11)$$

the number of electrons in the state **k**, σ; $f_{\mathbf{k}\sigma}$ has eigenvalues 0, 1. The lattice energy may be written

$$H_{\text{phon}}=\sum\hbar\omega_{\mathbf{w}}\,(b_{\mathbf{w}}{}^+b_{\mathbf{w}}+\tfrac{1}{2}), \qquad (2.12)$$

where $b_{\mathbf{w}}{}^+$, $b_{\mathbf{w}}$ are canonical Boson creation and destruction operators, satisfying the commutation rules

$$\left.\begin{aligned}[b_{\mathbf{w}}{}^+, b_{\mathbf{w}'}{}^+]=[b_{\mathbf{w}}, b_{\mathbf{w}'}]=0,\\ [b_{\mathbf{w}}, b_{\mathbf{w}'}{}^+]=\delta_{\mathbf{w},\mathbf{w}'},\end{aligned}\right\} \qquad (2.13)$$

and $\hbar\omega_w=\hbar ws_0$ is the energy of a phonon; s_0 is the velocity of sound in the ion system in the absence of interactions (and may depend on w). The number of phonons of wave number **w** is

$$n_{\mathbf{w}}=b_{\mathbf{w}}{}^+b_{\mathbf{w}}. \qquad (2.14)$$

The lattice–electron interaction is

$$H_{\text{int}}=\mathrm{i}\sum_{\mathbf{w}}D_w\,(\rho_{\mathbf{w}}b_{\mathbf{w}}{}^+-\text{c.c.}) \qquad (2.15)$$

where c.c. denotes the complex conjugate of the preceding quantity,

$$D_w{}^2 = \frac{4C^2\hbar\omega_w}{9N\Omega M s_0{}^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.16)$$

and $\rho_{\mathbf{w}}$ is the Fourier coefficient of the electron density,

$$\rho_{\mathbf{w}} = \sum_{\mathbf{k},\sigma} a_{\mathbf{k}-\mathbf{w},\sigma}{}^{+} a_{\mathbf{k}\sigma}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.17)$$

It is convenient to introduce the dimensionless coupling constant†

$$F = \Omega \Xi D_w{}^2/\hbar\omega_w, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.18)$$

where the number of energy levels per unit energy per unit volume at the Fermi surface is

$$\Xi = (2\pi)^{-2}\left\{k^2 \Big/ \left(\frac{\mathrm{d}\epsilon_k}{\mathrm{d}k}\right)\right\}_{k_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.19)$$

Finally, in (2.8), the Coulomb term

$$H_{\text{Coulomb}} = \sum_{\mathbf{q}} (2\pi e^2/q^2)\,\rho_{\mathbf{q}}{}^{+}\rho_{\mathbf{q}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.20)$$

has been included for completeness. Its role will be discussed in § 3.4.

A useful simplification is the 'quasi-free' electron approximation. The single-particle energy ϵ_k is taken to be quadratic in k, $\epsilon_k = A + \hbar^2k^2/2m$, where m is an effective mass. Umklappprozesse will be neglected, and the Bloch wave functions $\exp(i\mathbf{k}\,.\,\mathbf{r})\,u(\mathbf{r})$ replaced by free particle wave functions $\exp i(\mathbf{k}\,.\,\mathbf{r})$. Strictly, this simplification is not consistent, since if $u(\mathbf{r}) = 1$, then from (2.7)

$$C = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.21)$$

and there is no interaction. If however one regards C as a fixed constant, then the simplification may be made. In (2.9), (2.10), $a_{\mathbf{k}\sigma}{}^{+}, a_{\mathbf{k}\sigma}$ are now to be regarded as creation and destruction operators for free particles of mass m, and $\epsilon_k = \hbar^2k^2/2m$. In the quasi-free electron model, the density of levels (2.19) takes the form

$$\Xi = \tfrac{3}{4}N_e/\zeta_0 = \tfrac{3}{4}\nu N/\zeta_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.22)$$

where N_e = number of free electrons per unit volume, ν = number of free electrons per atom. The problem of the interaction of electrons with lattice vibrations has now been formulated completely as a field theory.

2.3. *Perturbation Theory*

The role of H_{int} (2.15), in the first place, was to produce real transitions between Bloch states, necessary for the ideal resistance of normal metals. Besides producing real transitions, however, it will lead (through virtual transitions) to a modification of the energy eigenstates. If it were not for the fact that the Bloch states are highly degenerate (forming as they do a three-dimensional continuum), there would be no difficulty in treating the interaction as a small perturbation. In the actual system, with its degeneracy, one must first find appropriate linear combinations of the Bloch wave functions to lift the degeneracy†.

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† This F differs from that of Fröhlich (1950, 1952, 1954) by a factor ν, the number of free electrons per atom.

Nevertheless, we might hope to get some qualitative and order-of-magnitude indications by simply writing down the usual second order energy perturbation, neglecting the presence of degeneracy (Fröhlich 1950):

$$\Delta E = -\sum_{\mathbf{k},\mathbf{q},\sigma} f_{\mathbf{k}\sigma}(1-f_{\mathbf{q}\sigma})\,|D_w{}^2|/(\epsilon_k-\epsilon_q+\hbar\omega_w), \quad . \quad . \quad (2.23)$$

where $\mathbf{w}=\mathbf{k}-\mathbf{q}$. The term in $f_{\mathbf{k}}$,

$$\Delta E_1 = -\sum_{\mathbf{k},\mathbf{q},\sigma} f_{\mathbf{k}\sigma}\,|D_w|^2/(\epsilon_k-\epsilon_q+\hbar\omega_w) \quad . \quad . \quad . \quad (2.24)$$

simply leads to a renormalization of the energy levels, but the term in $f_{\mathbf{k}}f_{\mathbf{q}}$,

$$\Delta E_2 = \sum_{\mathbf{k},\mathbf{q},\sigma} f_{\mathbf{k}\sigma}f_{\mathbf{q}\sigma}\,|D_w|^2/(\epsilon_k-\epsilon_q+\hbar\omega_w) \quad . \quad . \quad . \quad (2.25)$$

represents a dynamic interaction between electrons. It will be shown that this expression merely represents the diagonal part of the effective electron–electron interaction, and that the non-diagonal matrix elements will be much more important.

If the interaction is sufficiently strong it may be that the Bloch ground state is no longer the lowest state of the system ; some sort of condensation may occur. Clearly, the larger the interaction constant $F\,(\propto|D_w|^2)$, the greater is the likelihood of existence of a ground state differing from the Bloch ground state. In other words, the higher the normal resistance, the more favourable for the occurrence of superconductivity. One can estimate the order of magnitude of the energy of the condensed state by noting that small energy denominators, and hence large contributions to ΔE, occur only when $|\epsilon_k-\epsilon_q|\lesssim\hbar\omega_0$. Moreover, only Bloch states within $\sim\hbar\omega_0$ of the Fermi surface can be involved in the condensation, since otherwise the increase in kinetic energy of the electrons will be unprofitable. Hence, if $\hbar\bar{\omega}$ is an average phonon energy,

$$\begin{aligned}\Delta E_2 &\sim \sum_{\substack{|\epsilon_k-\zeta_0|<\hbar\bar{\omega}\\|\epsilon_q-\zeta_0|<\hbar\bar{\omega}}} |D_w{}^2|/\hbar\bar{\omega}\\ &\sim \Xi^2\Omega^2(\hbar\bar{\omega})^2C^2/NMs_0{}^2\Omega\\ &\sim N_e\Omega(C^2/\zeta_0)(m/M) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.26)\end{aligned}$$

(remembering that the maximum wave number $w_0\sim k_0$, so that $\hbar\bar{\omega}\sim\hbar k_0s_0$). The expression (2.26) shows the isotope effect, since $\Delta E_2\propto m/M$, $H_c\propto M^{-1/2}$. The smallness of the superconducting energy compared with the Fermi energy arises also, from the factor m/M; $\Delta E_2 \sim \hbar\bar{\omega}$ per electron†. This prediction is still too large, by a factor between 10 and 100, compared with observed condensation energies.

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† If the system does not become a superconductor, then perturbation theory, with the Bloch wave functions as the unperturbed states, should be reliable. The electron-phonon interaction makes a contribution to the linear term in the specific heat (Buckingham 1951, Buckingham and Schafroth 1954).

Bardeen (1950) proposed the use of a linear combination of a chosen Bloch wave function and all the other Bloch states that it can interact with in first order in the interval $|\epsilon_k - \zeta| \lesssim \hbar\bar{\omega}$ as a new basic wave function; he hoped that such wave functions would exhibit superconducting properties. This approach was formulated variationally, and was shown to lead to energy expressions essentially the same as Fröhlich's (Bardeen 1951).

2.4. *Renormalization of the Phonon Energy and Coupling Strength*

The indications from perturbation theory suggest that there is a critical value for F, below which superconductivity cannot arise. Although this suggestion turns out not to be true (see §§ 3.2, 3.3), it has stimulated some valuable investigations. If indeed F were large enough for the perturbation theory to give a new ground state, then (Wentzel 1951) application of perturbation theory to the energy of a phonon gives a negative total energy, implying lattice instability. It has been shown by Huang (1951) and Fröhlich (1952) that this feature arises, in a perturbative treatment, from the neglect of a possible adiabatic adjustment of the lattice to the motion of the electrons. To allow for this possibility, a canonical transformation will be performed; new field variables will be introduced, to decouple the electrons from the lattice motion as completely as possible (Fröhlich 1952, Nakajima 1953, Bardeen and Pines 1955).

Let

$$S_{\mathbf{w}} = \sum_{\mathbf{k},\sigma} g_{\mathbf{k},\mathbf{w}} (a_{\mathbf{k},\sigma}{}^{+} a_{\mathbf{k}-\mathbf{w},\sigma} b_{\mathbf{w}} + \text{c.c.}) \quad . \quad . \quad . \quad . \quad (2.27)$$

and

$$S = \sum_{\mathbf{w}} S_{\mathbf{w}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.28)$$

where $g_{\mathbf{k},\mathbf{w}}$ is a real c-number, to be determined. The unitary operator $\exp \mathrm{i} s$ is used to transform the Hamiltonian,

$$\begin{aligned} H^T &= \exp(-\mathrm{i}S) H \exp(\mathrm{i}S) \\ &= H + \mathrm{i}[H, S] - [[H, S], S]/2! + \ldots \quad . \quad . \quad . \quad . \quad (2.29) \end{aligned}$$

To evaluate (2.29), the following commutators are required:

$$[H_{\text{el}}, S] = \sum_{\mathbf{k},\mathbf{w},\sigma} (\epsilon_k - \epsilon_{|\mathbf{k}-\mathbf{w}|}) g_{\mathbf{k},\mathbf{w}} \{a_{\mathbf{k},\sigma}{}^{+} a_{\mathbf{k}-\mathbf{w},\sigma} b_{\mathbf{w}} - \text{c.c.}\}, \quad . \quad (2.30)$$

$$[H_{\text{phon}}, S] = \sum_{\mathbf{k},\mathbf{w},\sigma} \hbar\omega_w g_{\mathbf{k},\mathbf{w}} \{b_{\mathbf{w}}{}^{+} a_{\mathbf{k}-\mathbf{w},\sigma}{}^{+} a_{\mathbf{k},\sigma} - \text{c.c.}\}, \quad . \quad . \quad . \quad . \quad (2.31)$$

$$\begin{aligned} [\rho_w, S] = \sum_{\mathbf{k},\mathbf{w},\sigma} (f_{\mathbf{k}-\mathbf{w},\sigma} - f_{\mathbf{k},\sigma}) \{g_{\mathbf{k},\mathbf{w}} b_{\mathbf{w}}{}^{+} + \text{c.c.}\} \\ + \text{terms non-diagonal in electron variables}, \quad . \quad (2.32) \end{aligned}$$

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† For a fuller discussion of the qualitative features of the perturbation theoretical approach, see Fröhlich (1953) and the discussion on Fröhlich's paper.

$$\begin{aligned}[D_w\rho_{\mathbf{w}}b_{\mathbf{w}}^+ - \text{c.c.}, S] &= \sum_{\mathbf{w}} D_w(b_{\mathbf{w}}[\rho_{\mathbf{w}}^+, S] + [b_{\mathbf{w}}^+, S]\rho_{\mathbf{w}}^+ - \text{c.c.}) \\ &= \sum_{\mathbf{k},\mathbf{w},\sigma} D_w(f_{\mathbf{k}\sigma} - f_{\mathbf{k}-\mathbf{w},\sigma})g_{\mathbf{k},\mathbf{w}}(b_{\mathbf{w}}^+ + b_{\mathbf{w}}) \\ &\quad + \sum D_w g_{\mathbf{k},\mathbf{w}}(a_{\mathbf{k}-\mathbf{w},\sigma}{}^+ a_{\mathbf{k}\sigma}\rho_{\mathbf{w}}^+ + \text{c.c.}). \qquad \ldots \quad (2.33)\end{aligned}$$

With these commutators (2.29) gives

$$\begin{aligned}H^T = H_{\text{el}} + H_{\text{phon}} &+ \mathrm{i}\sum_{\mathbf{k},\mathbf{w},\sigma}\{D_w + g_{\mathbf{k},\mathbf{w}}(\epsilon_k - \epsilon_{|\mathbf{k}-\mathbf{w}|} - \hbar\omega_w)\}\{b_{\mathbf{w}}a^+{}_{\mathbf{k}\sigma}a_{\mathbf{k}-\mathbf{w},\sigma} - \text{c.c.}\} \\ &+ \sum_{\mathbf{k},\mathbf{w},\sigma}\{D_w g_{\mathbf{k},\mathbf{w}} + \tfrac{1}{2}g_{\mathbf{k}\mathbf{w}}{}^2(\epsilon_k - \epsilon_{|\mathbf{k}-\mathbf{w}|} - \hbar\omega_w)\} \\ &\times\{(f_{\mathbf{k}\sigma} - f_{\mathbf{k}-\mathbf{w},\sigma})(b_{\mathbf{w}}^+b_{\mathbf{w}} + b_{\mathbf{w}}b_{\mathbf{w}}^+) - (\rho_{\mathbf{w}}a_{\mathbf{k}-\mathbf{w},\sigma}{}^+a_{\mathbf{k}\sigma} + \text{c.c.})\} \\ &+ \text{higher order terms.} \qquad \ldots \quad (2.34)\end{aligned}$$

The coefficients $g_{\mathbf{k},\mathbf{w}}$ are to be chosen so as to eliminate terms linear in $b_{\mathbf{w}}^+$, $b_{\mathbf{w}}$ in H^T, i.e.

$$g_{\mathbf{k},\mathbf{w}} = D_w/(\epsilon_{|\mathbf{k}-\mathbf{w}|} - \epsilon_k - \hbar\omega_w). \qquad \ldots \quad (2.35)$$

However, the series development (2.29) is only valid if the coefficients $g_{\mathbf{k},\mathbf{w}}$ remain finite—an 'energy shell' must therefore be excluded from the transformation, i.e. we must take $g_{\mathbf{k},\mathbf{w}} = 0$ if $|\epsilon_{|\mathbf{k}-\mathbf{w}|} - \epsilon_k| < \Delta$, say. It can be shown (Fröhlich 1952, Bardeen and Pines 1955) that Δ can be chosen both large enough for rapid convergence of the expansion (2.29) and small enough to have negligible influence on the renormalization. Henceforth the restriction that (2.35) holds only for $|\epsilon_{|\mathbf{k}-\mathbf{w}|} - \epsilon_k| < \Delta$ will be weakened to the restriction that when a simple pole occurs in a summand or integrand, the principal value is to be understood.

With this understanding, (2.34) now gives

$$\begin{aligned}H^T = \sum_{\mathbf{k},\sigma}\epsilon_k a_{\mathbf{k}\sigma}{}^+a_{\mathbf{k}\sigma} &+ \sum_{\mathbf{w}}\hbar\tilde{\omega}_w(b_{\mathbf{w}}^+b_{\mathbf{w}} + \tfrac{1}{2}) + \mathrm{i}\sum_{\substack{\text{energy shell}\\ \text{only}}} D_w(\rho_{\mathbf{w}}b_{\mathbf{w}}^+ - \text{c.c.}) \\ &- \tfrac{1}{2}\sum_{\mathbf{k},\mathbf{w},\sigma}{}' \frac{D_w{}^2}{\epsilon_{|\mathbf{k}-\mathbf{w}|} - \epsilon_k + \hbar\omega_w}(\rho_{\mathbf{w}}a_{\mathbf{k}-\mathbf{w},\sigma}{}^+a_{\mathbf{k}\sigma} + \text{c.c.}) + \text{higher order terms,} \\ &\qquad \ldots \quad (2.36)\end{aligned}$$

where the terms neglected in (2.36) are at least quadratic and non-diagonal in the $b_{\mathbf{w}}^+$, $b_{\mathbf{w}}$ and can be neglected, to within the validity of the harmonic approximation for the lattice waves. The prime on the summation denotes the principal value, and

$$\begin{aligned}\tilde{\omega}_w &= \omega_w - \sum_{\mathbf{k},\mathbf{w},\sigma}{}' D_w g_{\mathbf{k},\mathbf{w}}(f_{\mathbf{k}\sigma} - f_{\mathbf{k}-\mathbf{w},\sigma}) \\ &\simeq \omega_w - 2\sum_{\mathbf{k},\mathbf{w},\sigma}{}' D_w{}^2\bar{f}_{\mathbf{k}\sigma}/(\epsilon_{|\mathbf{k}-\mathbf{w}|} - \epsilon_k) \qquad \ldots \quad (2.37)\end{aligned}$$

is the renormalized frequency. To within the present approximation, $\hbar\omega_w$ in the denominator may be replaced by $\hbar\tilde{\omega}_w$ everywhere; in (2.37) it is good enough to neglect the $\hbar\omega$ in the denominator entirely, and replace $f_{\mathbf{k}\sigma}$ by its expectation value. The observed velocity of sound, s, is $\tilde{\omega}_w/w$.

In terms of the renormalized coupling constant $\tilde{F}_w$, defined by

$$\tilde{F}_w/F = \omega_w/\tilde{\omega}_w = s_0/s, \qquad (2.38)$$

$$\begin{aligned} H^T = & \sum_{\mathbf{k},\sigma} \epsilon_k a_{\mathbf{k}\sigma}{}^+ a_{\mathbf{k}\sigma} + \sum_{\mathbf{w}} \hbar\tilde{\omega}_{\mathbf{w}} (b_{\mathbf{w}}{}^+ b_{\mathbf{w}} + \tfrac{1}{2}) \\ & + \mathrm{i} \sum_{\text{energy shell}} (D_w \rho_{\mathbf{w}}{}^+ b_{\mathbf{w}} - \text{c.c.}) \\ & + \sum_{\mathbf{k},\mathbf{w},\sigma}{}' \frac{\tilde{F}(\hbar\tilde{\omega}_w)^2 a_{\mathbf{k}\sigma}{}^+ a_{\mathbf{k}-\mathbf{w},\sigma} \rho_{\mathbf{w}}}{\Omega\Xi\{(\epsilon_{|\mathbf{k}-\mathbf{w}|} - \epsilon_k)^2 - (\hbar\tilde{\omega}_w)^2\}} + \text{higher order terms.} \end{aligned} \qquad (2.39)$$

Wentzel's difficulty is resolved, for it is F which has to be less than a critical value ~ 1 for lattice stability, while $\tilde{F}$, which appears in an electron–electron interaction term, may be as large as we please.

This renormalization may also be derived by Bogoliubov's transformation. The advantage of that method is that it leaves the Hamiltonian in a rather more convenient form for determining the ground state. Since, however, even the 'weak coupling' limit $F \to 0$ will lead to superconductivity, the renormalization is not essential in principle. It will be necessary for a completely quantitative theory, since in fact for most metals F is not very small, compared with unity. In the weak coupling limit, the interaction terms in (2.39),

$$H' = \sum_{\mathbf{k},\mathbf{w},\sigma}{}' \frac{\tilde{F}(\hbar\tilde{\omega}_w)^2 a_{\mathbf{k}\sigma}{}^+ a_{\mathbf{k}-\mathbf{w},\sigma} \rho_{\mathbf{w}}}{\Omega\Xi\{(\epsilon_{|\mathbf{k}-\mathbf{w}|} - \epsilon_k)^2 - (\hbar\tilde{\omega}_w)^2\}} \qquad (2.40)$$

are just the second order perturbation matrix elements.

The Coulomb interaction (2.20) has, so far, been neglected entirely. Following Bohm and Pines (1953), we may introduce additional coordinates for the collective (plasma) modes of the system, together with constraints to preserve the correct number of degrees of freedom of the system. Then a Bohm–Pines transformation, to decouple the plasma and individual particle modes, leads to a 'screened' Coulomb interaction, of short range. Nakajima (1953) and Bardeen and Pines (1953) included the Coulomb interaction in this way, and subjected it to the transformation (2.29), resulting in the appearance on the right-hand side of (2.39) of the additional term

$$\sum_{k>k_c} \frac{4\pi e^2}{k^2} \rho_{\mathbf{k}}{}^+ \rho_{\mathbf{k}}. \qquad (2.41)$$

The Bohm and Pines approach is not rigorous enough for this result to be completely convincing, however. Further discussion of the Coulomb interaction will be given in § 3.4.

The Hamiltonian (2.39) serves as the starting point for the work of Bardeen, Cooper and Schrieffer (§ 3.2). It exhibits an explicit electron–electron interaction. The diagonal part is just the energy ΔE of (2.23) but there are many non-diagonal terms of (2.40), of the same order of magnitude as the diagonal ones. The actual expressions are modified by Bardeen *et al.*, to simplify the calculation.

§ 3. THE GROUND STATE AND ENERGY GAP

3.1. *Fröhlich's one-dimensional Model*

The difficulty in the perturbation theory (§ 2.3) arises from the degeneracy of the Bloch states (Fröhlich 1953). Perturbation theory alters the effective mass of electrons near the Fermi surface, but does not greatly affect the density of states for low-lying excited states; one would expect the lifting of the degeneracy to modify the density of states considerably. Experimentally the absence of any term in the specific heat linear in the temperature shows that the density of low-lying states is greatly reduced. The most recent measurements of the specific heat of tin (Corak *et al.* 1954, 1956, Corak and Satterthwaite 1956, Lynton *et al.* 1957, Zavaritskiî 1957) confirm the suggestion (Ginsburg 1946, Koppe 1947, 1950, Goodman 1953) that there is an actual energy gap between the ground state and the lowest excited states.

An electron within $\sim\hbar\omega_0$ of the Fermi surface can emit a phonon and reabsorb it, returning to its original state. These are the only processes considered in the second-order energy perturbation expression. But having emitted this quantum it could, instead, absorb any of the other phonons present, ending in any of about $\Xi\Omega\,.\,\hbar\bar{\omega}$ states. The probability that any given one of these phonons is excited is fairly small, $\sim(\hbar\bar{\omega}/\zeta_0)^{1/2}$, but the probability that the electron absorbs a *different* phonon is overwhelming compared with the probability that it absorbs the phonon that it, itself, emitted (and the ratio is proportional to the volume (Fröhlich 1953)).

If the coupling is strong enough, one might get very high excitation of a very small number of lattice modes; if so the degeneracy is greatly reduced. To try to get some qualitative understanding of the 'condensation', Fröhlich (1954) examined an extreme case—a one-dimensional metal with exceedingly large $\tilde{F}$. The difficulties are associated with the high density of states, which is greatly reduced in one dimension. Further, in view of the Pauli exclusion principle, the only possible resonances are between electrons at opposite ends of the Fermi sea. If the energy of recoil is neglected, then the lattice modes $\pm w_0$ $(w_0=2k_0)$ are strongly excited, since they are exactly the modes required to produce resonance. It is assumed that all other lattice modes can be regarded as a perturbation; this assumption is only valid if the coupling constant $\tilde{F}$ is quite unrealistically large. A particle representation will be used in this section, since the physical mechanism will be clearer than in second quantization.

If for the present all lattice modes other than $\pm w_0$ are neglected, then, with a Hartree self-consistent field approximation, the Schrödinger equation separates into the single-electron equations

$$(p_j+\mathrm{i}\{D_{w_0}(\bar{b}_{w_0}+\bar{b}^{+}{}_{-w_0})\exp(\mathrm{i}w_0x_j)-\text{c.c.}\})\,\psi_k(x_j)=E_k\psi_k(x_j) \qquad (3.1)$$

together with the lattice equations

$$\left.\begin{aligned}&\{\hbar\omega_{w_0}b_{w_0}{}^{+}b_{w_0}+\mathrm{i}\,N_e\Omega D_{w_0}(b_{w_0}{}^{+}\overline{\exp(\mathrm{i}w_0x)}-\text{c.c.})\}\chi_{w_0}=\lambda_{+}\,\chi_{w_0},\\&\{\hbar\omega_{w_0}b_{-w_0}{}^{+}b_{-w_0}+\mathrm{i}\,N_e\Omega D_{w_0}(b_{-w_0}{}^{+}\overline{\exp(-\mathrm{i}w_0x)}-\text{c.c.})\}\chi_{-w_0}=\lambda_{-}\,\chi_{-w_0}.\end{aligned}\right\} \quad . \quad . \quad . \quad (3.2)$$

Equations (3.2) are Schrödinger equations for oscillators referred to a displaced origin, and it follows at once that

$$\begin{aligned}\bar{b}_{\pm w_0} &= \pm\mathrm{i}\,(D_{w_0}/\hbar\omega_{w_0})\,N_e\Omega\,\overline{\exp(\mp\mathrm{i}w_0x)}\\ &= \pm\mathrm{i}\,(D_{w_0}/\hbar\omega_{w_0})\sum_k\int\mathrm{d}x\,\psi_k{}^*(x)\exp(\mp\mathrm{i}w_0x)\psi_{k-}(x).\end{aligned} \quad . \quad (3.3)$$

Equation (3.3) connecting the electron and phonon variables, provides a condition of self-consistency. In it the integration is over the normalization volume Ω, and the summation is over all occupied states k.

(3.1) describes a single electron in a sinusoidal field—the very situation which gives rise to the band structure in solids; an energy gap results precisely as in band theory. If $k \simeq k_0$, then the solutions of the Schrödinger equation are

$$\left.\begin{aligned}\psi_{k-} &= \Omega^{-1/2}\,(u_k{}^{1/2}\exp(\mathrm{i}kx) + v_k{}^{1/2}\exp[\mathrm{i}(k-w_0)x+\mathrm{i}\beta]),\\ \psi_{k+} &= \Omega^{-1/2}\,(v_k{}^{1/2}\exp(\mathrm{i}kx) + u_k{}^{1/2}\exp[\mathrm{i}(k-w_0)x+\mathrm{i}\beta])\end{aligned}\right\} \quad . \quad (3.4)$$

where β is a phase angle, k is to be taken greater than zero, u_k, v_k real,

$$u_k{}^2 = \tfrac{1}{2}\,(1+\eta_k/\sqrt{(\eta_k{}^2+\Gamma^2)}), \quad . \quad . \quad . \quad . \quad . \quad (3.5)$$

$$u_k{}^2 + v_k{}^2 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.6)$$

and

$$\Gamma = \tfrac{1}{2}D_{w_0}\,|\,\bar{b}_{w_0} + \bar{b}_{-w_0}{}^+|. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.7)$$

The single particle energy, relative to the Fermi surface is (Peierls 1930)

$$\xi_{k\pm} = \tfrac{1}{2}(\eta_k+\eta_{k-w_0}) \pm \sqrt{[(\eta_k-\eta_{k-w_0})^2+\Gamma^2]} \quad . \quad . \quad . \quad (3.8)$$

(where $\xi_k = E_k - \zeta_0$, $\eta_k = \epsilon_k - \zeta_0$). There is clearly an energy gap 2Γ between the ground state and all excited states.

Although the expressions (3.4), (3.5) and (3.8) are valid only near $k = k_0$, they can be extended to all k by perturbation theory (Fröhlich 1954). The perturbative corrections are negligible in determining Γ, since it is the k near k_0 that are important. But when k is not near k_0, either u_k or v_k is nearly unity, and the other is small, of order Γ/ζ. Then the perturbations arising from transitions between k and $k+w_0$ or $k-w_0$ and $k-2w_0$ are comparable with the smaller term in (3.4). For k_- states, the perturbative corrections are

$$\left.\begin{aligned}\Delta\psi_{k-} &= \frac{\tfrac{1}{2}\Omega^{-1/2}\Gamma\exp[\mathrm{i}(k+w_0)x-\mathrm{i}\beta]}{\zeta_0(1+k/k_0)}, \quad \Delta E_{k-} = \frac{\Gamma^2}{\zeta_0(1+k/k_0)}\,;\ k<k_0,\\ \Delta\psi_{k-} &= \frac{\tfrac{1}{2}\Omega^{-1/2}\Gamma\exp[\mathrm{i}(k-2w_0)x+\mathrm{i}\beta]}{\zeta_0(3-k/k_0)}, \quad \Delta E_{k-} = \frac{\Gamma^2}{\zeta_0(3-k/k_0)}\,;\ k>k_0.\end{aligned}\right\} \quad (3.9)$$

The quantity $\overline{\exp(\mathrm{i}w_0x)}$ appearing in (3.3) is

$$\begin{aligned}\overline{\exp(\mathrm{i}w_0x)} &= (N_e\Omega)^{-1}\sum_{\substack{\text{occupied } k\\ (\text{i.e. all } k-)}}\int\psi_{k-}{}^*\exp(\mathrm{i}w_0x)\,\psi_{k-}\,\mathrm{d}x\\ &= (N_e\Omega)^{-1}\sum\frac{\mathrm{i}\Gamma\exp(\mathrm{i}\beta)}{2\sqrt{(\Gamma^2+\eta_k{}^2)}}\end{aligned} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.10)$$

To evaluate this expression, use is made of the fact that in the ground state the k_- states are occupied and the k_+ states unoccupied. The one-dimensional expression for converting sums over occupied k to integrals is

$$\sum_{\text{occupied } k} \ldots = \tfrac{1}{2} N_e \Omega k_0^{-1} \int_0^{2k_0} \mathrm{d}k \ldots, \qquad (3.11)$$

with the aid of which (3.10) is

$$\overline{\exp(\mathrm{i}w_0 x)} = \tfrac{1}{2}\mathrm{i}\,(\Gamma/\zeta_0)\exp(\mathrm{i}\beta)\ln(4\zeta_0/\Gamma) \qquad (3.12)$$

(assuming the smallness of Γ compared to ζ_0). Substituting (3.7) and (3.12) in (3.3) gives

$$\tfrac{2}{3}F\ln(4\zeta_0/\Gamma) = 1 \quad \text{or} \quad \Gamma = 0. \qquad (3.13)$$

The non-trivial solution is the one of lower energy, and gives for Γ

$$\Gamma = 4\zeta_0 \exp(-3/2F). \qquad (3.14)$$

The total energy, measured from the Bloch ground state is (from (3.3), (3.8), (3.9), (3.10) and (3.14)),

$$\begin{aligned} W &= 2\sum_k \xi_{k-} + \hbar\omega_{w_0}(\bar{b}_{w_0}^{+}\bar{b}_{w_0} + \bar{b}_{-w_0}^{+}\bar{b}_{-w_0}) \\ &= -8N_e\Omega\zeta_0\exp(-3/F). \end{aligned} \qquad (3.15)$$

In the calculation of W, there are two comparable contributions—a large shift (of order Γ) of a small fraction ($\sim \Gamma/\zeta_0$) of the energy levels, and a small shift ($\sim \Gamma^2/\zeta_0$) of the other levels. For the latter, the perturbative corrections (3.9) are important.

The calculation can be extended to a finite temperature (Kuper 1955). merely replacing expectation values by ensemble averages. Excited electrons are in k_+ states, and reduce the amplitude of the electron density wave

$$\sum_i \exp(\mathrm{i}w_0 x_i)$$

and hence also of the lattice displacement, $|\bar{b}_{w_0} + \bar{b}_{-w_0}^{+}|$. The gap $2\Gamma(T)$ is a monotonically falling function of temperature, and vanishes at a temperature $\kappa T_0 = 1{\cdot}14\Gamma$; above this temperature the Bloch states are restored. The specific heat is exponential in $2\Gamma/\kappa T$ at low temperatures, and has an Ehrenfest (1933) second-order transition at T_0. The magnitude of $\Gamma(T)$ is proportional to the intensity of the lattice displacements, and serves as an analogue to the 'internal field' of the Weiss (1907) theory of ferromagnetism.

The expression (3.15) for the condensation energy does *not* show any isotope effect. This is a consequence of the fact that the recoil energy of the lattice has been neglected—the $b_{\pm w_0}^{+}$, $b_{\pm w_0}$ have been treated as *classical* field variables. A condition for the validity of this approximation is that the gap must be so large that *no* other phonon mode w can cause an electron to bridge it, i.e. $\hbar\omega_{\max} < 2\Gamma$. But the total condensation energy per electron $\sim \kappa T_0$. The condition may therefore be written

$$T_c > \Theta \qquad (3.16)$$

(where Θ is the Debye temperature), which is not satisfied by any real metal. The method cannot be generalized either to weaker interactions or to three dimensions, and its main value therefore lies in showing that the electron–phonon interaction *can* produce a condensation, and in suggesting the exponential dependence of the energy on the coupling constant—a result which of course cannot arise in any finite order perturbation theory.

3.2. *The Three-dimensional Model of Bardeen, Cooper and Schrieffer*

The one-dimensional model has shown the possibility of finding a solution not expressible in a power series—$\exp(-1/F)$ has an essential singularity at $F=0$ and cannot be expanded. In addition $\exp(-1/F)$ is a very sensitive function of F, and if it arises in the three-dimensional theory it would explain the wide scatter of superconducting critical temperatures (e.g. Shoenberg 1952), and also the large pressure coefficient (Kan *et al.* 1948, Chester and Jones 1953, Muench 1955, Lüthi and Rohrer 1958) of the critical temperature; if the factor $\exp(-1/F)$ can be combined with the 'isotope effect' factor $(\hbar\bar{\omega})^2$ of (2.26), many of the objectives of the theory are fulfilled.

The renormalized Hamiltonian (2.39) exhibits an explicit electron–electron interaction which is negative (attractive) when the interacting electrons have energies differing by less than $\sim\hbar\tilde{\omega}_{w\max}$, positive (repulsive) otherwise. Clearly the ground state should be one in which the attractions are as effective as possible, and the repulsions as ineffective as possible. One might even hope that in the ground state the repulsive interactions might be negligible. If this guess should prove correct, then it is possible to simplify the Hamiltonian considerably without loss of any essential features. This is the approach of Bardeen *et al.* (1957)—they replace $\tilde{\omega}_{\mathbf{w}}$ by an average value $\bar{\omega}$ and simplify the interaction (2.40)

$$H'=\frac{\tilde{F}}{\Xi\Omega}\sum_{\substack{\mathbf{k},\mathbf{q},\mathbf{w},\\ \sigma,\sigma'}} G(\epsilon_k-\epsilon_{|\mathbf{k}-\mathbf{w}|})a_{\mathbf{k},\sigma}{}^{+}a_{\mathbf{k}-\mathbf{w},\sigma}a_{\mathbf{q}+\mathbf{w},\sigma'}{}^{+}a_{\mathbf{q},\sigma'} \quad . \quad (3.17)$$

by taking (broken curve, see figure)

$$\left.\begin{aligned} G&=-1, \ |\epsilon_k-\epsilon_{|\mathbf{k}-\mathbf{w}|}|<\hbar\bar{\omega}, \\ G&=0, \quad |\epsilon_k-\epsilon_{|\mathbf{k}-\mathbf{w}|}|>\hbar\bar{\omega}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3.18)$$

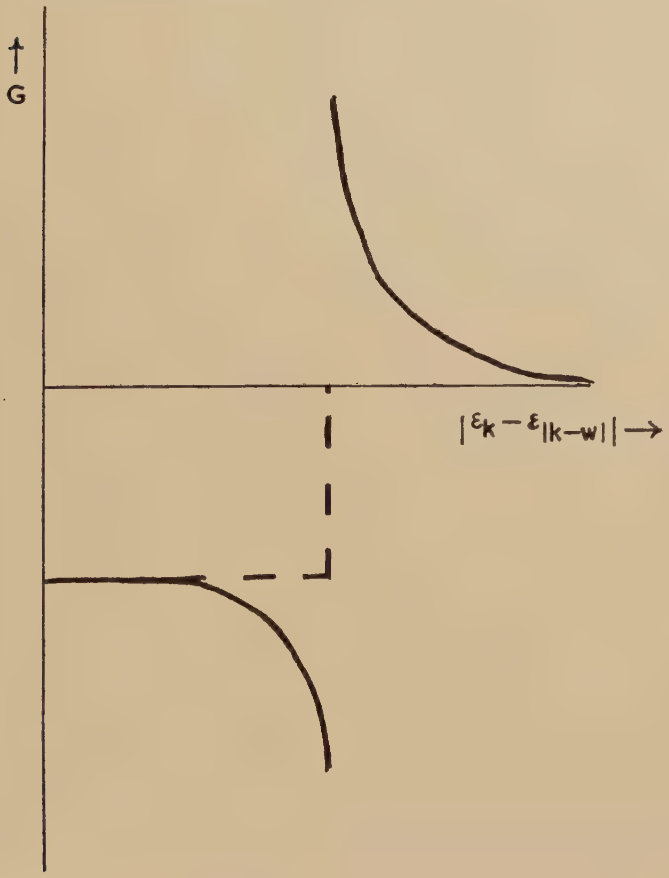
instead of the actual expression (continuous curve, see figure)

$$G=\frac{(\hbar\bar{\omega})^2}{(\epsilon_{|\mathbf{k}-\mathbf{w}|}-\epsilon_k)^2-(\hbar\bar{\omega})^2}. \quad . \quad . \quad . \quad . \quad . \quad (3.19)$$

This inter-electron attraction makes it possible for electrons near the Fermi surface to condense into quasi-molecular pairs with zero total net momentum, as conjectured by Schafroth *et al.* (1957). Cooper (1956) calculated the binding energy and wave function of one of these pairs, however, and found that the diameter of a quasi-molecule is $\sim 10^{-4}$ cm; the overlap of quasi-molecules is important and prevents us from treating the system of pairs as an ideal Bose gas. Let us consider a single state ϕ_0, of energy ϵ_0, of the electron pair, interacting through a constant matrix element V with $N\Omega$ states ϕ_n, energies ϵ_n, in a narrow energy shell of thickness $\sim h\omega$. Then the Schrödinger equation for the state $\psi = \sum c_n\phi_n + c_0\phi_0$ may be written

$$c_0\epsilon_0\phi_0 + \sum c_n V\phi_n = Ec_0\phi_0\,, \qquad (3.20)$$

$$c_n\epsilon_n\phi_n + c_0 V\phi_0 = E\,c_n\phi_n. \qquad (3.21)$$



There are two types of solution. If $c_0 = 0$, then from (3.21), $E = \epsilon_n$ and hence from (3.20)

$$\sum c_n V\phi_n = 0. \qquad (3.22)$$

This is a single restriction on the $N\Omega$ coefficients c_n, so that there will be $N\Omega - 1$ solutions of this type with energies in the shell. The other two solutions are outside the continuum. If $E \neq \epsilon_n$ is assumed, then from (3.21)

$$c_n = Vc_0\phi_0/(E - \epsilon_n)\phi_n \qquad (3.23)$$

so that, from (3.20)

$$\begin{aligned} E-\epsilon_0 &= V^2\sum(E-\epsilon_n)^{-1} \\ &= \Xi\Omega V^2\int_{\epsilon_0-\frac{1}{2}\hbar\omega}^{\epsilon_0+\frac{1}{2}\hbar\omega} d\epsilon/(E-\epsilon) \\ &= -\Xi\Omega V^2 \ln\left|(E-\epsilon_0-\tfrac{1}{2}\hbar\omega)/(E-\epsilon_0+\tfrac{1}{2}\hbar\omega)\right|, \qquad (3.24) \end{aligned}$$

where Ξ is the density of states (per unit volume). One of these states, the Cooper quasi-molecule, lies below the continuum (as may easily be seen in the particular case of an infinitely thin energy shell, when (3.24) reduces to a quadratic equation for E).

The situation with many electrons is rather more complicated—the Pauli exclusion principle prevents one from simply pairing off all the electrons in Cooper pairs in a straightforward way. There is however one way in which it can be done fairly easily: all the pairs must have the same net momentum, and for the ground state this momentum must of course be zero. When exchange effects are taken into account, the antiparallel spin correlations are favoured compared to parallel spins.

For the moment, only *some* of the non-diagonal terms of the interaction will be considered—those in which (see (3.17)) $\mathbf{k}-\mathbf{w}=-\mathbf{q}:\sigma=\sigma'$. These terms scatter the pair ($\mathbf{q}, \uparrow$; $-\mathbf{q}, \downarrow$) into ($\mathbf{k}, \uparrow$; $-\mathbf{k}, \downarrow$). This 'reduced' interaction Hamiltonian, of course, contains only a small fraction of the number of terms in (3.17). However *all* pairs ($\mathbf{k}, \uparrow$; $-\mathbf{k}, \downarrow$) are connected by terms in H_{reduced} and all terms *not* included in H_{reduced} will break pair correlations. The simplest improvement on the Bloch wave functions would seem to be functions containing two-body correlations but no higher ones; for such functions, H_{reduced} will play an important role but $H'-H_{\text{reduced}}$ will not.

It is convenient to consider a state which is not an eigenstate of the total number of particles $N_e\Omega=\sum a_{\mathbf{k}\sigma}{}^{+}a_{\mathbf{k}\sigma}$, i.e. the number of particles is not precisely specified. Since $\sum a_{\mathbf{k}\sigma}{}^{+}a_{\mathbf{k}\sigma}$ commutes with the Hamiltonian, the exact ground state is certainly an eigenstate of $N_e\Omega$. If necessary, we may always take the projection of the approximate ground state on to the subspace of $N_e\Omega$ particles.

As a variational *ansatz*, consider the wave function of Bardeen *et al.* (1957) (where $|0\rangle$ is the electron vacuum)

$$\Psi=\prod_{\mathbf{k}}(u_k+v_k a_{\mathbf{k}\uparrow}{}^{+}a_{-\mathbf{k}\downarrow}{}^{+})|0\rangle. \qquad (3.25)$$

It exhibits the desired pairwisec orrelations, and the parameters u_k, v_k will be chosen to minimize the energy, subject to the normalization condition

$$u_k{}^2+v_k{}^2=1. \qquad (3.26)$$

Symmetry will be assumed between electrons above the Fermi surface and holes below it, i.e. $u_k+v_{k'}=1$ if $\epsilon_k+\epsilon_{k'}=2\zeta_0$. In terms of energies measured from the Fermi surface,

$$\eta_k=\epsilon_k-\zeta_0, \qquad (3.27)$$

the expectation kinetic energy for the state (3.25) is

$$2\sum_{\eta_k>0}\eta_k v_k^2 + 2\sum_{\eta_k<0}|\eta_k|u_k^2, \qquad . \; . \; . \; . \; . \; . \tag{3.28}$$

and the expectation interaction energy is

$$\frac{\tilde{F}}{\Omega\Xi}\sum_{\mathbf{k},\mathbf{k}'} u_k v_k u_{k'} v_{k'} G(\eta_k-\eta_{k'}). \qquad . \; . \; . \; . \; . \; . \tag{3.29}$$

Only those terms in H' contribute which belong to H_{reduced}, i.e. in which the pairwise correlations remain unbroken; the remaining terms of H' have zero expectation value. Minimization of the expectation value of the energy leads to an integral equation for u_k, v_k

$$4v_k\eta_k + \sum u_{k'}v_{k'}(\tilde{F}/\Omega\Xi)G(\eta_k-\eta_{k'})\{(u_k^2-v_k^2)/u_k\}=0,$$

i.e. replacing the sum by an integral in the usual way,

$$4\eta_k u_k v_k = (u_k^2-v_k^2)\tilde{F}\int u_{k'}v_{k'}G(\eta_k-\eta_{k'})\,\mathrm{d}\eta_{k'}. \qquad . \; . \tag{3.30}$$

This integral equation is difficult to solve as it stands, even with the simplified interaction (3.18). For that reason the further simplification of Bardeen *et al.*,

$$\left.\begin{aligned} &G=1 \quad \text{if} \quad |\eta_k|<\hbar\bar{\omega},\ |\eta_{k'}|<\hbar\bar{\omega}, \\ &G=0 \quad \text{otherwise}, \end{aligned}\right\} \qquad . \; . \; . \; . \; . \tag{3.31}$$

will be made for the present. With this factorizable potential, the integral equation is

$$u_k v_k/(u_k^2-v_k^2) = (\tilde{F}/2\eta_k)\int_0^{\hbar\bar{\omega}} u_{k'}v_{k'}\,\mathrm{d}\eta_{k'} \qquad . \; . \; . \; . \tag{3.32}$$

which is easily solved. The solution is (where evidently the + sign is appropriate for $\eta_k<0$)

$$u_k^2 = \tfrac{1}{2}(1\mp\eta_k/\sqrt{(\eta_k^2+\Gamma^2)}), \qquad . \; . \; . \; . \; . \; . \tag{3.33}$$

$$\Gamma = (\tilde{F}/\Omega\Xi)\sum_{k'} u_{k'}v_{k'} = \hbar\bar{\omega}\,\operatorname{cosech}(1/\tilde{F}), \quad . \; . \; . \; . \; . \tag{3.34}$$

giving for the ground state energy (taking the normal state as zero)

$$W = -2\Xi\Omega(\hbar\bar{\omega})^2/(\exp(2/\tilde{F})-1). \quad . \; . \; . \; . \; . \; . \tag{3.35}$$

However weak the electron–lattice coupling (provided only $\tilde{F}>0$), the ground state of Bardeen *et al.* has a lower energy than the Bloch ground state. (This result is to be contrasted with the perturbation theory, which only gave a distinct ground state if $\tilde{F}$ was sufficiently large.) In the limit of weak coupling

$$\Gamma = 2\hbar\bar{\omega}\exp(-1/\tilde{F}), \quad . \; . \; . \; . \; . \; . \; . \; . \; . \tag{3.36}$$

$$W = -\Omega\Xi(\hbar\bar{\omega})^2\exp(-2/\tilde{F}). \quad . \; . \; . \; . \; . \; . \tag{3.37}$$

Wave functions for low-lying excited states can be constructed by similar arguments, and Bardeen *et al.* showed that there is an energy gap 2Γ between the ground state and any 'single-particle' excited state. The derivation of the excitation spectrum is most easily performed by the method of Bogoliubov (1958a, b), and will accordingly be deferred to § 3.3.

Besides these particle excitations, collective (current carrying) excitations can be generated, by building up states in which the pairing is $(\mathbf{k}, \uparrow\ ; -\mathbf{k}+\mathbf{q}, \downarrow)$, where $\mathbf{q}$ is a constant. These states will have essentially the same interaction energy as the ground state, and will differ from it only by the kinetic energy of the electron current. In contrast, any single particle excitation breaks the coupling of an electron to all the Cooper pairs, producing the finite energy gap.

With the accurate form (3.19) for the interaction, the integral equation is more difficult to solve. What one can do fairly simply instead, is to use the solution (3.33), (3.34), in (3.25), as a trial wave function, with the accurate expression (3.19) for the interaction Hamiltonian ; Γ is regarded as a parameter to be chosen to minimize the energy (Kuper 1958). In the weak coupling limit, the exponential dependence of the ground state energy on $\tilde{F}^{-1}$ is again found, though with some slight numerical differences. At the same time, that method shows that the diagonal terms of (3.17) are not important.

The results of the theory of Bardeen *et al.* (3.36) and (3.37) resemble (3.14) and (3.15) of the one-dimensional theory, with the 'isotope-effect' factor $\hbar\bar{\omega}$ in place of ζ_0. This is just the combination needed to reconcile the isotope effect and the need for a very sensitive parameter. Moreover, if $\tilde{F}$ is even moderately small, $\exp(-1/\tilde{F})$ may be very small, explaining why $T_0 \ll \Theta$ rather than $T_0 \sim \Theta$, as one might otherwise expect. For real superconductors, the relation between T_0 and Θ suggests $\tilde{F} \sim \frac{1}{4}$. $\tilde{F}$ is fairly small, so that the weak coupling limit should be a reasonable first approximation.

In the one-dimensional theory, if T_0 is not $\gtrsim \Theta$, the approximation method fails. Qualitatively it can no longer be true that only one pair of lattice modes is excited ; instead we expect a narrow range of wave numbers near k_0 to contribute. A finite range of coherence may be expected, since the resonant lattice vibration should have the form of a wave packet of finite extent instead of a plane wave.

In the light of the results of Bardeen *et al.* one might make the *ad hoc* restriction in the one-dimensional case that only states within $\hbar\bar{\omega}$ of the Fermi surface should be taken into account in producing the gap (that is to say electrons *not* within $\sim\hbar\bar{\omega}$ of the surface follow the lattice adiabatically). In that case, all integrals should be restricted by the condition

$$|k-k_0|/k_0 < \tfrac{1}{2}\hbar\bar{\omega}/\zeta_0.$$

Equation (3.10) is modified to read

$$\begin{aligned}\overline{\exp(\mathrm{i}w_0x)} &= (N_e\Omega)^{-1} \sum_{|\eta_k| < \hbar\bar{\omega}} \tfrac{1}{2}\mathrm{i}\Gamma \exp(\mathrm{i}\beta)/\sqrt{(\Gamma^2+\eta_k{}^2)} \\ &= (2k_0)^{-1} \int_{k_0(1-\hbar\bar{\omega}/2\zeta_0)}^{k_0(1+\hbar\bar{\omega}/2\zeta_0)} \mathrm{i}\Gamma \exp(\mathrm{i}\beta)\mathrm{d}k/2\sqrt{(\Gamma^2+\eta_k{}^2)} \\ &= \tfrac{1}{2}\mathrm{i} \exp(\mathrm{i}\beta)(\Gamma/\zeta_0)\ln(2\hbar\bar{\omega}/\Gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3.38)\end{aligned}$$

assuming $\Gamma \ll 2\hbar\bar{\omega}$. Hence, in place of (3.13) we have

$$\tfrac{2}{3}F \ln (2\hbar\bar{\omega}/\Gamma) = 1 \quad \text{or} \quad \Gamma = 0,$$

the former alternative giving

$$\Gamma = 2\hbar\bar{\omega} \exp(-3/2F). \qquad (3.39)$$

Although (3.36) and (3.39) are formally almost identical, the wave functions are very different. In terms of second quantization operators the transformation leading to the wave function (3.4) of the one-dimensional model is of the form

$$\left.\begin{aligned} \alpha_{k-,\,s} &= u_k{}^{1/2} a_{ks} + \exp(\mathrm{i}\beta) v_k{}^{1/2} a_{k-w_0,\,s'} \\ \alpha_{k+,\,s} &= v_k{}^{1/2} a_{ks} + \exp(\mathrm{i}\beta) u_k{}^{1/2} a_{k-w_0,\,s'} \end{aligned}\right\} \qquad (3.40)$$

with no mixing of creation and destruction operators (cf. (3.41)). The wave function is always an eigenstate of particle number.

Indeed the apparent non-conservation of particle number in the three-dimensional theory lies behind the difficulty in forming a physical picture of an 'internal field', such as one has in one dimension (a difficulty which, in turn, is responsible for the difficulty (§ 4.2) in constructing a theory of the electromagnetic properties). If we wish to form an excited particle, we ought, simultaneously, to produce an excited hole. The electrons which have to be displaced in k-space, together with the lattice displacement that they carry with them adiabatically, produce the internal field. In the wave function (3.25), with an indefinite number of particles, this picture is lost, since the wave function does not contain information concerning where an electron has 'come from'.

An intrinsic drawback of all variational methods is that there is no internal criterion for the accuracy of the solutions. Moreover the Hamiltonian (2.39) to which the method is applied is itself only correct up to order F. Since the solutions are not expressible in a power series in F, it is not obvious that they have any significance applied to the original Hamiltonian (2.8). The trial wave function (3.25) is designed to use only a small subset of the terms in the (renormalized) interaction, and it is at least possible that a more complicated wave function might have considerably lower energy. For all these reasons, a systematic method of approximation is desirable, in place of the *ad hoc* method of this section: the 'quasi-particle' transformation of Bogoliubov (1958 a, b), to be described in § 3.3, provides this systematic approach.

3.3. *Bogoliubov's 'quasi-particle' Transformation*

The considerations outlined in § 3.2 make the existence of a condensed state very plausible, and give the desirable exponential dependence of the condensation energy on $1/F$. So many approximations and simplifications are however needed that the method fails to be completely convincing. The best justification, as well as the simplest derivation of the excitation spectrum, follows from the 'quasi-particle' transformation (Bogoliubov

1958 a, b, Valatin 1958). This is an extension of Bogoliubov's (1947) Boson quasi-particle transformation (see (3.66)) developed originally for the study of the superfluidity of helium. Let us define†

$$\left.\begin{aligned} \alpha_{\mathbf{k}+} &= u_k a_{\mathbf{k}\uparrow} - v_k a_{-\mathbf{k}\downarrow}{}^+, \\ \alpha_{\mathbf{k}+}{}^+ &= u_k a_{\mathbf{k}\uparrow}{}^+ - v_k a_{-\mathbf{k}\downarrow}, \\ \alpha_{\mathbf{k}-} &= u_k a_{\mathbf{k}\downarrow} + v_k a_{-\mathbf{k}\uparrow}{}^+, \\ \alpha_{\mathbf{k}-}{}^+ &= u_k a_{\mathbf{k}\downarrow}{}^+ + v_k a_{-\mathbf{k}\uparrow}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.41)$$

with

$$u_k = u_{-k},\ v_k = v_{-k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.41')$$

It is easily verified that the $\alpha_{\mathbf{k}\pm}{}^+$, $\alpha_{\mathbf{k}\pm}$ variables satisfy canonical Fermion anticommutation rules, provided the real numbers u_k, v_k satisfy (cf. (3.6), (3.26))

$$u_k{}^2 + v_k{}^2 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.42)$$

A particular choice of the u_k, v_k, which gives familiar results is

$$\left.\begin{aligned} u_k = 1,\ v_k = 0 \quad &\text{if} \quad \epsilon_k > \zeta_0; \\ u_k = 0,\ v_k = 1 \quad &\text{if} \quad \epsilon_k < \zeta_0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.43)$$

With this choice, $\alpha_{\mathbf{k}+}{}^+$ represents a creation operator for an electron ($\mathbf{k}, \uparrow$) if $\epsilon_k > \zeta_0$, and for a hole ($-\mathbf{k} \downarrow$) if $\epsilon_k < \zeta_0$.

The transformation (3.41) does not conserve particle number. To take account of particle number conservation,

$$\mathscr{N} \equiv \sum_{\mathbf{k},\,\sigma} a_{\mathbf{k}\sigma}{}^+ a_{\mathbf{k}\sigma} = N_e \Omega, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.44)$$

a term $-\zeta\mathscr{N}$ is included in the Hamiltonian, where the chemical potential ζ is determined by the condition that the *expectation* number of particles

$$\overline{\mathscr{N}} = N_e \Omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.45)$$

In terms of these new variables, the Hamiltonian (2.8) becomes (still neglecting the Coulomb term)

$$H = \mathscr{A} + H_0 + H_1 + H_2 + H_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.46)$$

where

$$\mathscr{A} = 2 \sum_{\mathbf{k}} (\epsilon_k - \zeta) v_k{}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.47)$$

$$\begin{aligned} H_0 = {} & \sum_{\mathbf{k}} (\epsilon_k - \zeta)(u_k{}^2 - v_k{}^2)\{\alpha_{\mathbf{k},+}{}^+ \alpha_{\mathbf{k},+} + \alpha_{\mathbf{k},-}{}^+ \alpha_{\mathbf{k},-}\} \\ & + \sum_{\mathbf{w}} \hbar\omega_w (b_{\mathbf{w}}{}^+ b_{\mathbf{w}} + \tfrac{1}{2}), \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.48)$$

$$H_1 = 2 \sum (\epsilon_k - \zeta) u_k v_k \{\alpha_{\mathbf{k},+}{}^+ \alpha_{\mathbf{k},-}{}^+ + \alpha_{-\mathbf{k},-} \alpha_{\mathbf{k},+}\}, \quad . \quad . \quad . \quad . \quad . \quad (3.49)$$

$$\begin{aligned} H_2 = \mathrm{i} \sum_{\mathbf{k},\,\mathbf{w}} D_w \{ & u_k v_{|\mathbf{k}+\mathbf{w}|} (\alpha_{\mathbf{k},+}{}^+ \alpha_{-\mathbf{k}-\mathbf{w},-}{}^+ + \alpha_{-\mathbf{k}-\mathbf{w},+}{}^+ \alpha_{\mathbf{k},-}{}^+) \\ & + u_{|\mathbf{k}+\mathbf{w}|} v_k (\alpha_{-\mathbf{k},-} \alpha_{\mathbf{k}+\mathbf{w},+} + \alpha_{\mathbf{k}+\mathbf{w},-} \alpha_{-\mathbf{k},+})\} b_{\mathbf{w}}{}^+ - \text{c.c.} \end{aligned} \quad . \quad . \quad (3.50)$$

$$\begin{aligned} H_3 = \mathrm{i} \sum_{\mathbf{k},\,\mathbf{w}} D_w \{ & u_k u_{|\mathbf{k}+\mathbf{w}|} (\alpha_{\mathbf{k},+}{}^+ \alpha_{\mathbf{k}+\mathbf{w},+} + \alpha_{\mathbf{k},-}{}^+ \alpha_{\mathbf{k}+\mathbf{w},-}) \\ & - v_k v_{|\mathbf{k}+\mathbf{w}|} (\alpha_{-\mathbf{k}-\mathbf{w},-}{}^+ \alpha_{-\mathbf{k},-} + \alpha_{-\mathbf{k}-\mathbf{w},+}{}^+ \alpha_{-\mathbf{k},+})\} b_{\mathbf{w}}{}^+ - \text{c.c.} \end{aligned} \quad . \quad (3.51)$$

---

† The notation differs slightly from Bogoliubov, and helps to make explicit the conservation of wave vector.

Two procedures have been used for the selection of the parameters u_k, v_k. One may again proceed variationally, selecting u_k, v_k to minimize the expectation energy—this is Valatin's method. It depends on knowing the general character of the ground state, in the same way as the method of Bardeen *et al.* The alternative, due to Bogoliubov (1958 a), will be developed here. It has the advantage of yielding the form of the ground state. Valatin's approach will prove useful in § 3.5, in the study of the thermal properties of the system.

If we attempt a perturbation calculation, difficulties arise on account of vanishing energy denominators. The 'dangerous' denominators are those in which two quasi-particles are created from vacuum and no phonons, and do not arise before transformation, below fourth order. Bogoliubov's method consists in selecting the parameters u_k, v_k so that the 'dangerous' denominators do not arise. In principle one would like to suppress them in all orders. In actual fact we will merely arrange for their cancellation in second order. This proves sufficient, since an energy gap appears in the excitation spectrum. Higher order processes are therefore unlikely to contribute 'dangerous' denominators after the transformation is completed.

The terms H_1, creating two quasi-particles without phonons, are 'dangerous' already in first order. On the other hand, H_3 conserves quasi-particle number, merely creating or destroying a phonon, and H_2 creates or destroys two quasi-particles with emission or absorption of a phonon. Hence in second order there is a 'dangerous' process in which H_2 creates two quasi-particles and a phonon, and H_3 absorbs the phonon and scatters one of the quasi-particles. Bogoliubov's method arranges for the mutual compensation of these two 'dangerous' processes. Writing $|V\rangle$ for the quasi-particle 'vacuum' (i.e. the ground state of H_0) we require

$$\{H_1 - H_3 H_0^{-1} H_2\}|V\rangle = 0, \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (3.52)$$

i.e.

$$2(\epsilon_k - \zeta)u_k v_k = \sum_{\mathbf{w}} D_w^{\,2} \frac{u_{|\mathbf{k}+\mathbf{w}|} v_{|\mathbf{k}+\mathbf{w}|}(u_k^2 - v_k^2) - (u_{|\mathbf{k}+\mathbf{w}|}^2 - v_{|\mathbf{k}+\mathbf{w}|}^2) u_k v_k}{E_k + E_{|\mathbf{k}+\mathbf{w}|} + \hbar\omega_w}, \qquad (3.53)$$

defining

$$\left.\begin{aligned} E_k &= (\epsilon_k - \zeta)(u_k^2 - v_k^2) = \eta_k(u_k^2 - v_k^2), \\ \tilde{E}_k &= \tilde{\eta}_k(u_k^2 - v_k^2), \\ \tilde{\eta}_k &= \eta_k - \sum_{\mathbf{w}} D_w^2 (u_{|\mathbf{k}+\mathbf{w}|}^2 - v_{|\mathbf{k}+\mathbf{w}|}^2)/(E_k + E_{|\mathbf{k}+\mathbf{w}|} + \hbar\omega_w). \end{aligned}\right\} \quad . \quad . \qquad (3.54)$$

Replacing the $\eta_k = \epsilon_k - \zeta$ in the denominator by $\tilde{\eta}_k$ (making an error of fourth order only in the D_w), and converting the sum to an integral, this gives

$$\tilde{\eta}_k u_k v_k = \{\Omega/(2\pi)^3\}(u_k^2 - v_k^2) \int \frac{D_w^2 u_{|\mathbf{k}+\mathbf{w}|} v_{|\mathbf{k}+\mathbf{w}|} \mathrm{d}^3 w}{\tilde{E}_k + \tilde{E}_{|\mathbf{k}+\mathbf{w}|} + \hbar\omega_w}, \quad . \qquad (3.55)$$

an integral equation (cf. (3.30)) to determine u_k, v_k. Besides the trivial solution $u_k v_k = 0$, it has another one, the one leading to the superconducting state. Guided by the simplified solution (3.33), (3.34) we may define

$$\Gamma(k) = \frac{\Omega}{(2\pi)^3} \int \frac{D_w{}^2 u_{|\mathbf{k}+\mathbf{w}|} v_{|\mathbf{k}+\mathbf{w}|} \mathrm{d}^3 w}{\tilde{E}_k + \tilde{E}_{|\mathbf{k}+\mathbf{w}|} + \hbar\omega_w} \quad . \quad . \quad . \quad . \quad (3.56)$$

to find

$$\left.\begin{aligned} u_k{}^2 &= \tfrac{1}{2}\{1 + \tilde{\eta}_k/(\tilde{\eta}_k{}^2 + \Gamma(k)^2)^{1/2}\} \\ v_k{}^2 &= \tfrac{1}{2}\{1 - \tilde{\eta}_k/(\tilde{\eta}_k{}^2 + \Gamma(k)^2)^{1/2}\} \end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad (3.57)$$

From (3.55) $\Gamma(k)$ satisfies the integral equation

$$\Gamma(k) = \frac{\Omega}{(2\pi)^3} \int \frac{D_w{}^2 \Gamma(|\mathbf{k}+\mathbf{w}|) \mathrm{d}^3 w}{(\tilde{E}_k + \tilde{E}_{|\mathbf{k}+\mathbf{w}|} + \hbar\omega_w)\sqrt{(\Gamma^2(|\mathbf{k}+\mathbf{w}|) + \tilde{\eta}_{|\mathbf{k}+\mathbf{w}|}{}^2)}} . \qquad (3.58)$$

For weak coupling ($F \rightarrow 0$), this equation has an asymptotic solution exponential in F^{-1}, as may be seen thus: It will be assumed that $\Gamma(k)$ is a slowly varying function, and can be regarded as constant in the range $0 < \tilde{\eta}_k < \hbar\omega_0$; moreover the $\hbar\omega_w$ will be replaced by an average value $\hbar\bar{\omega}$ (cf. § 3.2). Then from (3.58)

$$\Gamma(k) = \tilde{F} \int_0^{\hbar\bar{\omega}} \frac{\hbar\bar{\omega}}{\tilde{E}_k + \tilde{E}_{|\mathbf{k}+\mathbf{w}|} + \hbar\omega_w} \frac{\Gamma(|\mathbf{k}+\mathbf{w}|) \mathrm{d}\tilde{\eta}_{|\mathbf{k}+\mathbf{w}|}}{\sqrt{(\Gamma^2(|\mathbf{k}+\mathbf{w}|) + \tilde{\eta}_{\mathbf{k}+\mathbf{w}}{}^2)}} . \qquad (3.59)$$

The main contribution to the right hand side arises when $\tilde{\eta}_{|\mathbf{k}+\mathbf{w}|} \lesssim \frac{1}{2}\hbar\bar{\omega}$ (since for $\tilde{\eta}_{|\mathbf{k}+\mathbf{w}|} \gtrsim \frac{1}{2}\hbar\bar{\omega}$ the $\tilde{\eta}_{|\mathbf{k}+\mathbf{w}|}$ in the denominator dominates). Within the important region, $\tilde{\eta}_{|\mathbf{k}+\mathbf{w}|}$ will be neglected compared to $\hbar\bar{\omega}\sqrt{(\Gamma^2 + \tilde{\eta}^2{}_{|\mathbf{k}+\mathbf{w}|})}$, enabling the $\hbar\bar{\omega}$ to be cancelled, giving

$$\begin{aligned} \Gamma = F \int_0^{\frac{1}{2}\hbar\bar{\omega}} \frac{\Gamma \mathrm{d}\tilde{\eta}}{\sqrt{(\Gamma^2 + \tilde{\eta}^2)}} &= \Gamma F \int_0^{\frac{1}{2}\hbar\bar{\omega}/\Gamma} \mathrm{d}s/\sqrt{(1+s^2)} \\ &= \Gamma F \ln \hbar\bar{\omega}/\Gamma, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.60) \end{aligned}$$

i.e.

$$\Gamma = \hbar\bar{\omega} \exp(-1/F). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.61)$$

The chemical potential ζ is determined by the condition that the total number of particles should have expectation value $N_e\Omega$—this gives, in good approximation, $\zeta = \zeta_0$.

The integral equation for Γ can be solved without the approximation of constant ω, and gives the same result, with an explicit expression for the average $\bar{\omega}$. Apart from a factor 2 in (3.61), the resulting expressions for $\Gamma(k)$, u_k, v_k are identical with those of Bardeen *et al.* (see (3.34) and (3.35)). The ground state, expressed in the new variables, is of course the quasi-particle vacuum. Expressed in real electron variables, it is just (3.25), as can easily be seen by verifying that $\alpha_{\mathbf{k},\sigma}$ annihilates the state (3.25).

The energy of the ground state will now be calculated, without the approximations of Bardeen, Cooper and Schrieffer. It is

$$W = \mathscr{A} - \langle V|H_2 H_0{}^{-1} H_2|V\rangle . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.62)$$

H_3 gives no contribution to the ground state energy in second order, as it creates and destroys a particle; while H_1, which creates two particles, has already been compensated (to second order in the wave functions) by the consecutive action of H_2 and H_3. The expression (3.62) is very similar in form to that of Bardeen *et al.*, since the matrix elements of $H_2 H_0^{-1} H_2$ between Bloch states are just the matrix elements of the renormalized interaction used by Bardeen. The evaluation of the energy is straightforward, using the expressions (3.57), (3.61) and gives (Bogoliubov 1958 a)

$$W = -\tfrac{1}{2}(\hbar\bar{\omega})^2 \Omega \Xi \exp(-2/F), \quad . \quad . \quad . \quad . \quad . \quad (3.63)$$

in agreement with (3.37), if $\bar{\omega}$ is replaced by $2\bar{\omega}$ (cf. (3.61)).

The elementary excitations of the system are generated by the quasi-particle creation operators $\alpha_{\mathbf{k}\sigma}{}^{+}$, out of the ground state. The energy $\mathscr{E}_k$ of a quasi-particle with wave number $\mathbf{k}$ is, to second order,

$$\begin{aligned}\mathscr{E}_k &= \langle V|\alpha_{\mathbf{k}\sigma}(H-\zeta\mathscr{N})\alpha_{\mathbf{k}\sigma}{}^{+}|V\rangle - \langle V|\alpha_{\mathbf{k}\sigma}H_3(H_0-E_k)^{-1}H_3\alpha_{\mathbf{k}\sigma}{}^{+}|V\rangle \\ &= \tilde{E}_k\left\{1-\sum_{\mathbf{w}}\frac{D_w{}^2(u_k{}^2 u_{|\mathbf{k}+\mathbf{w}|}{}^2+v_k{}^2 v_{|\mathbf{k}+\mathbf{w}|}{}^2)}{(\tilde{E}_{|\mathbf{k}+\mathbf{w}|}+\hbar\omega_w)^2-\tilde{E}_k{}^2}\right\} \\ &\quad +2\sum_{\mathbf{w}}\frac{u_k v_k u_{|\mathbf{k}+\mathbf{w}|} v_{|\mathbf{k}+\mathbf{w}|} D_w{}^2(\tilde{E}_{|\mathbf{k}+\mathbf{w}|}+\hbar\omega_w)}{(E_{|\mathbf{k}+\mathbf{w}|}+\hbar\omega_w)^2-E_k{}^2}. \quad . \quad . \quad (3.64)\end{aligned}$$

The first sum vanishes as $k \to k_0$, on account of the factor $\tilde{E}_k$, but the second remains finite and near the Fermi surface tends to

$$\begin{aligned}&2u_k v_k \sum_{\mathbf{w}} u_{|\mathbf{k}+\mathbf{w}|} v_{|\mathbf{k}+\mathbf{w}|} D_w{}^2/(E_{|\mathbf{k}+\mathbf{w}|}+\hbar\omega_w) \\ &\qquad \sim 2u_k v_k \Gamma(k) \sim \Gamma(k_0) = \hbar\bar{\omega}\exp(-1/F). \quad . \quad . \quad . \quad (3.65)\end{aligned}$$

Thus quasi-particle excitations have energies separated from the ground state by $\Gamma(k_0)$; to create a quasi-particle pair requires at least $2\Gamma(k_0)$. As in the simplified theory, there are also low-lying current-carrying states, which will be discussed in § 4.1, since they are important in understanding the difference between a superconductor and an insulator.

The above calculation has used Fröhlich's unrenormalized Hamiltonian. Bogoliubov (1958 b) has shown that similar results may be obtained from the renormalized Hamiltonian, using the same transformation. The most satisfactory procedure, however, is to carry out a Boson transformation (Bogoliubov 1947) on the phonon variables

$$\left.\begin{aligned}\beta_{\mathbf{k}} &= \lambda_k b_{\mathbf{k}} + \mu_k b_{-\mathbf{k}}{}^{+}, \\ \beta_{\mathbf{k}}{}^{+} &= \lambda_k b_{\mathbf{k}}{}^{+} + \mu_k b_{-\mathbf{k}}, \\ \lambda_k{}^2 - \mu_k{}^2 &= 1,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.66)$$

simultaneously with the Fermion transformation (3.41) (Bogoliubov *et al.* 1958 a). Using the condition that in second order the terms $H_1+H_2+H_3$ do not contribute to the 'quasi-phonon' energy, the coefficients λ_k, μ_k are determined, and the expression (2.37) for the phonon frequencies is obtained. The calculation of electronic energy levels follows as above, with F replaced by $\tilde{F}$.

3.4. *The Role of Coulomb Interactions*

Qualitatively, it is very plausible that the Coulomb repulsions between electrons tend to prevent the formation of quasi-molecular pairs, and thus to hinder the occurrence of superconductivity, as suggested by Bardeen *et al.* A rigorous treatment of the Coulomb interaction is difficult, on account of the long range of the forces, but a rough order of magnitude can be obtained fairly easily.

It is well known (for example from the theory of a quantum mechanical plasma (Bohm and Pines 1953, Pines 1953, Bardeen and Pines 1955)) that the correlations between electrons lead to a 'screening' of the interaction†. For a preliminary discussion of the role of Coulomb interactions in superconductivity, the screened interaction (which is of short range) will be used instead of the complete unscreened form. The structure, in Fermion field operators, of the Coulomb interaction (2.20) is the same as that of the 'phonon' interaction between electrons (2.40), but with the very different function

$$\begin{aligned} G_c &= (3\Xi/4\tilde{F})2\pi e^2/w^2, \quad w > k_c \\ &= 0, \qquad\qquad\qquad\qquad w < k_c, \end{aligned} \qquad (3.67)$$

replacing G of (3.17). G_c is a very anisotropic function of $\mathbf{k}$, $\mathbf{k}+\mathbf{w}$ but in evaluating the expectation energy of an isotropic state such as (3.25), an angular average is implied. This average over angles is almost independent of the energies η_k, $\eta_{|\mathbf{k}+\mathbf{w}|}$ (measured from the Fermi surface) (Kuper 1958), since for the important terms, we already know that $\eta \lesssim \hbar\bar{\omega}$. The introduction of screening before taking the average over angles simplifies the calculation greatly; in the sixfold integral analogous to (3.29), no divergences occur. The particular Bohm–Pines form (3.67) for the screening is not essential. Any modification of the factor w^{-2}, preventing the divergence for small w, will suffice.

The constant (averaged) Coulomb matrix element can now be grouped with the interaction term (3.17) of the Bardeen–Cooper–Schrieffer calculation. A superconducting ground state will be expected only if $G_c < 1$ (since only then will $G + G_c$ be negative for sufficiently small η_k, $\eta_{|\mathbf{k}+\mathbf{w}|}$). The criterion for superconductivity is

$$\tilde{F} - A > 0 \qquad (3.68)$$

where A is

$$\begin{aligned} A &= \langle\{\tfrac{4}{3}\tilde{F}/\Xi\Omega\}G_c\rangle_{\text{Average}} \\ &\sim e^2\Xi/k_0{}^2, \end{aligned} \qquad (3.69)$$

since the cut-off k_c is comparable with k_0.

---

† Chester and Houghton (1959) have recently recalculated the phonon frequencies and interaction matrix elements, using a Born-Oppenheimer expansion in powers of $(m/M)^{1/4}$. The results are almost identical with those of Bardeen and Pines, and provide a rather better justification for the 'cut-off' Coulomb interaction.

For a more rigorous treatment, it is clearly necessary to start from the unscreened Coulomb interaction (2.20) and to transform it, together with all other terms of (2.8), under all canonical transformations that are to be applied. In a Bogoliubov transformation, the cancellation of all 'dangerous' processes must include those processes arising from the Coulomb interaction.

Applying the transformation (3.41) to H_{Coulomb} gives

$$H_{\text{Coulomb}} = \sum_{\substack{\mathbf{k},\mathbf{l},\mathbf{w},\\ s,s'}} \frac{2\pi e^2}{\Omega w^2} (u_k \alpha_{\mathbf{k}s}{}^{+} + v_k \alpha_{-\mathbf{k},-s})(u_{|\mathbf{k}-\mathbf{w}|,s}\alpha_{\mathbf{k}-\mathbf{w},s} + v_{|\mathbf{k}-\mathbf{w}|}\alpha_{-\mathbf{k}+\mathbf{w},-s}{}^{+})$$

$$\times (u_l \alpha_{\mathbf{l}s'}{}^{+} + v_l \alpha_{-\mathbf{l},-s'})(u_{|\mathbf{l}+\mathbf{w}|}\alpha_{\mathbf{l}+\mathbf{w},s'} + v_{|\mathbf{l}+\mathbf{w}|}\alpha_{-\mathbf{l}-\mathbf{w},-s'}{}^{+}). \quad . \quad (3.70)$$

The part of H_{Coulomb} diagonal in the a^+, a operators (i.e. the terms arising when $\mathbf{k}=\mathbf{l}+\mathbf{w}$, $s'=s$) is, expressed in terms of α^+, α,

$$H_{c_1} = 2 \sum_{\mathbf{k},\mathbf{l},s,} \{u_k{}^2 v_l{}^2 + (u_k{}^2 - v_k{}^2)(u_l{}^2 - v_l{}^2)\alpha_{\mathbf{k}s}{}^{+}\alpha_{\mathbf{k}s}\} 2\pi e^2/|\mathbf{k}-\mathbf{l}|^2\Omega$$

$$+ \text{ higher order terms.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.71)$$

The first term in (3.71) may be grouped with $\mathscr{A}$ (3.47) and the second with H_0 (3.48). Both these expressions are divergent, but the second diverges even in the 'normal' state. If, *ad hoc*, the w^{-2} is replaced by a 'screened' expression, these terms converge; moreover the value of $\mathscr{A}$ does not play any important role, while the contribution to H_0 is not very sensitive to small departures of u_k, v_k from the 'normal' values. This term will not be of importance in studying the difference between the normal and superconducting states. It will, rather, represent a further renormalization of the (normal) electronic energy levels. A full treatment is difficult, requiring a sum of a perturbation series, to infinitely high order (Gell-Mann and Brueckner 1957, Bogoliubov *et al.* 1958 a). There are no 'dangerous' terms in (3.71), however, since the summation over the two possible spin assignments cancels the quadratic terms non-diagonal in α^+, α. The only 'dangerous' part of (3.70) creating two quasi-particles from the ground state, arises when $\mathbf{k}=-\mathbf{l}$, $s=-s'$; this assignment leads to no diagonal terms,

$$H_{c_2} = \sum_{\mathbf{k},\mathbf{w}} \frac{2\pi e^2}{\Omega w^2} u_{|\mathbf{k}+\mathbf{w}|} v_{|\mathbf{k}+\mathbf{w}|} (u_k{}^2 - v_k{}^2)(\alpha_{\mathbf{k}+}{}^{+}\alpha_{-\mathbf{k},-}{}^{+} + \text{c.c}). \quad . \quad (3.72)$$

When the relevant terms of H_{c_1} and H_{c_2} are included, eqns. (3.47) (3.48) and (3.49) become (where the superscript c denotes the inclusion of Coulomb terms)

$$\mathscr{A}^c = 2 \sum_{\mathbf{k}} (\epsilon_k - \zeta) v_k{}^2 + 2 \sum_{\mathbf{k},\mathbf{l}} u_l{}^2 v_k{}^2 \,.\, 2\pi e^2/|\mathbf{k}-\mathbf{l}|^2\Omega, \quad . \quad . \quad . \quad . \quad . \quad (3.73)$$

$$H_0{}^c = \sum_{\mathbf{w}} \hbar\omega_w (b_{\mathbf{w}}{}^{+} b_{\mathbf{w}} + \tfrac{1}{2}) + \sum_{\mathbf{k},s} \alpha_{\mathbf{k}s}{}^{+}\alpha_{\mathbf{k}s} \{(\epsilon_k - \zeta)$$

$$+ \sum_{\mathbf{l}} (u_l{}^2 - v_l{}^2) \,.\, 2\pi e^2/|\mathbf{k}-\mathbf{l}|^2\Omega\}\{u_k{}^2 - v_k{}^2\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.74)$$

$$H_1{}^c = 2 \sum_{\mathbf{k}} \{(\epsilon_k - \zeta) u_k v_k + \sum_{\mathbf{l}} (2\pi e^2/|\mathbf{k}-\mathbf{l}|^2\Omega)(u_k{}^2 - v_k{}^2) u_l v_l\}$$

$$(\alpha_{\mathbf{k}+}{}^{+}\alpha_{-\mathbf{k},-}{}^{+} + \text{c.c.}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.75)$$

and H_2 and H_3 are unaffected. The (divergent) contribution to H_0^c will be assumed to have been included in the energies $\tilde{E}_k$. The compensation of 'dangerous' processes in second order gives, in place of (3.55),

$$\tilde{\eta}_k u_k v_k = (u_k^2 - v_k^2)\,.\,(2\pi)^{-3} \int \mathrm{d}^3 w \; u_{|\mathbf{k}+\mathbf{w}|} v_{|\mathbf{k}+\mathbf{w}|} \left\{ \frac{\Omega D_w^2}{\tilde{E}_k + \tilde{E}_{|\mathbf{k}+\mathbf{w}|} + \hbar\omega_w} - \frac{2\pi e^2}{w^2} \right\}, \qquad (3.76)$$

where in (3.76), all integrals converge, for both large and small w. The solutions for u_k, v_k are still given by (3.57). provided Γ is redefined,

$$\Gamma(k) = (2\pi)^{-3} \int \frac{\Gamma(|\mathbf{k}+\mathbf{w}|)\mathrm{d}^3 w}{(\Gamma^2(|\mathbf{k}+\mathbf{w}|) + \tilde{\eta}_{|\mathbf{k}+\mathbf{w}|}{}^2)^{1/2}} \left\{ \frac{\Omega D_w^2}{\tilde{E}_k + \tilde{E}_{|\mathbf{k}+\mathbf{w}|} + \hbar\omega_w} - \frac{2\pi e^2}{w^2} \right\}. \qquad (3.77)$$

With the same assumptions that were made in (3.60), the new equation (3.77) is solved by

$$\Gamma = (F - A) \int_0^{\hbar\bar{\omega}/2} \frac{\Gamma \,\mathrm{d}\tilde{\eta}}{\sqrt{(\Gamma^2 + \tilde{\eta}^2)}} \qquad (3.78)$$

where A is an appropriate average of $2\pi e^2/\Omega w^2$ and is clearly of the order of magnitude $\Xi e^2/k_0^2$ (cf. (3.69)). The criterion for superconductivity is once more given by eqn. (3.68).

The assumption of smallness of the Coulomb energy is not essential, but if it is not made, the perturbation series must be carried to infinite order. This, indeed, is what has to be done to avoid the divergences in (3.73), (3.74). Bogoliubov, Tolmachev and Shirkov have shown how this may be done, by the methods of Gell-Mann and Brueckner (1957) and Sawada (1957); the actual criterion for superconductivity is somewhat modified, and is more complicated than (3.68).

3.5. *The Energy Gap at Finite Temperatures*

When trying to calculate thermodynamic properties of a superconductor we can no longer use Bogoliubov's method, the compensation of 'dangerous' processes. At a finite temperature, real transitions can and do occur, and in any perturbation theory lead to vanishing denominators. They occur with so small a statistical weight, in an ensemble average, that a statistical mechanical perturbation theory for the free energy can be developed (Schafroth 1951, Nakajima 1955) and converges more strongly than the usual perturbation theory for the internal energy. No processes are 'dangerous' in Bogoliubov's sense.

The quasi-particle transformation can however still be used, with Valatin's approach. The coefficients u_k, v_k of (3.41) are selected to make the free energy a minimum. Thus at $T = 0$, we recover the results of §3.2. For simplicity, we consider the 'truncated' interaction

Hamiltonian (3.17), (3.31) of Bardeen *et al.* (1957)†. The coefficients u_k, v_k of the quasi-particle transformation (3.41) are unspecified, for the present, but we note that the states

$$\Big\{\prod_{\text{an arbitrary set of states }(\mathbf{k},\,s)} \alpha_{\mathbf{k}s}{}^{+}\Big\}|V\rangle$$

form a complete set. Provided the u_k, v_k are correctly chosen (e.g. Bogoliubov's choice as $T\to 0$), these multiple excitation states will be regarded as statistically independent. Here a self-consistent approximation has been implied, since the best choice u_k, v_k, and therefore the set of 'independent' quasi-particles, will depend on temperature.

It is convenient to denote the expectation number of quasi-particles in $(\mathbf{k}, s)$

$$\bar{f}_{\mathbf{k}s} = \langle \alpha_{\mathbf{k}s}{}^{+}\alpha_{\mathbf{k}s}\rangle_{\text{Ensemble average}}. \qquad (3.79)$$

Then the entropy is

$$S = \kappa \sum_{\mathbf{k},\,s} \{\bar{f}_{\mathbf{k},\,s} \ln \bar{f}_{\mathbf{k},\,s} + (1-\bar{f}_{\mathbf{k},\,s}) \ln (1-\bar{f}_{\mathbf{k}s})\}, \qquad (3.80)$$

on account of the statistical independence of the quasi-particle excitations.

The contribution of the state $(\mathbf{k}, s)$ to the expectation kinetic energy is $v_k{}^2\eta_k$, if there is *no* quasi-particle in the state. This follows because the wave function, $\prod_{\mathbf{k},\,s} \alpha_{\mathbf{k}s}|0\rangle$, expressed in terms of $a_{\mathbf{k}s}{}^{+}$, $a_{\mathbf{k}s}$ operators, contains the factor $(u_k a_{-\mathbf{k},\,-s} + v_k a_{\mathbf{k},\,s}{}^{+})$, i.e. the probability of a real electron in $(\mathbf{k}, s)$ is $v_k{}^2$. If there *is* a quasi-particle in the state, the wave function contains instead the factor $(v_k a_{-\mathbf{k},\,-s} - u_k a_{\mathbf{k},\,s}{}^{+})$; the probability for a real electron is $u_k{}^2$. These two configurations occur respectively with statistical weights $1-\bar{f}_{\mathbf{k}s}$, $\bar{f}_{\mathbf{k}s}$. Hence the expectation kinetic energy is

$$\sum_{\mathbf{k},\,s} \eta_k\{u_k{}^2\bar{f}_{\mathbf{k},\,s} + v_k{}^2(1-\bar{f}_{\mathbf{k},\,s})\}. \qquad (3.81)$$

With the factorizable potential (3.31) the pair of states $(\mathbf{k}, s)$, $(\mathbf{l}, s)$ contributes to the interaction energy an expression which is the product of $-\tilde{F}/\Omega\Xi$ and two factors, one from each state. If there is no quasi-particle in $(\mathbf{k}, s)$, the factor for state $(\mathbf{k}, s)$ (as in § 3.2) is $u_k v_k$ and if there is a quasi-particle, the factor is $-u_k v_k$. The weights of these states being $(1-\bar{f}_{\mathbf{k}s})$ and $\bar{f}_{\mathbf{k}s}$ respectively, the interaction energy is

$$-\sum_{\mathbf{k},\,\mathbf{l},\,s} (\tilde{F}/\Omega\Xi)(1-2\bar{f}_{\mathbf{k}s})(1-2\bar{f}_{\mathbf{l}s})u_k v_{\mathbf{k}} u_l v_l. \qquad (3.82)$$

---

† The following derivation and minimization of the free energy, due to Valatin (1958), is exactly equivalent to that of Bardeen *et al.* apart from the use of the quasi-particle notation. Bogoliubov *et al.* (1958 b) have rederived these results, using the quasi-particle transformation together with statistical mechanical perturbation theory.

The free energy is then

$$\begin{aligned}\mathscr{F} = & \sum_{\mathbf{k},s} \eta_k\{u_k^2\bar{f}_{\mathbf{k}s} + v_k^2(1-\bar{f}_{\mathbf{k}s})\} \\ & - \sum_{\mathbf{k},\mathbf{l},s} (\bar{F}/\Omega\Xi)u_k v_k u_l v_l(1-2\bar{f}_{\mathbf{k}s})(1-2\bar{f}_{\mathbf{l}s}) \\ & - \kappa T \sum_{\mathbf{k},s} \{\bar{f}_{\mathbf{k}s} \ln \bar{f}_{\mathbf{k}s} + (1-\bar{f}_{\mathbf{k}s}) \ln (1-\bar{f}_{\mathbf{k}s})\}, \quad . \quad . \quad . \quad (3.83)\end{aligned}$$

which has to be minimized with respect to u_k and $\bar{f}_{\mathbf{k}}$.

If $\Gamma(T)$ is defined by

$$\Gamma(T) = \sum_{\mathbf{k},s} (\bar{F}/\Omega\Xi)u_k v_k(1-2\bar{f}_{\mathbf{k},s}), \quad . \quad . \quad . \quad . \quad (3.84)$$

then the minimization with respect to u_k (or v_k) proceeds as in § 3.2, with $\Gamma(T)$ in place of Γ and gives

$$u_k^2 = \tfrac{1}{2}\{1 - \eta_k/\surd(\eta_k^2 + \Gamma^2(T))\}. \quad . \quad . \quad . \quad . \quad . \quad (3.85)$$

Substituting for u_k, v_k in (3.83), and minimizing with respect to $\bar{f}_{\mathbf{k},s}$ leads to

$$\kappa T\{\ln \bar{f}_{\mathbf{k}s} - \ln(1-\bar{f}_{\mathbf{k},s})\} + \surd(\eta_k^2 + \Gamma^2(T)) = 0, \quad . \quad . \quad . \quad (3.86)$$

i.e.

$$\bar{f}_{\mathbf{k}} = \{1 + \exp(\surd[\eta_k^2 + \Gamma^2(T)]/\kappa T)\}^{-1}, \quad . \quad . \quad . \quad . \quad (3.87)$$

an ideal Fermi gas distribution, with an energy spectrum $\surd(\eta_k^2 + \Gamma^2(T))$. With the solutions for u_k, v_k, and $\bar{f}_{\mathbf{k}}$, (3.84) describes an explicit temperature dependence of the energy gap $2\Gamma(T)$. As in the one-dimensional case, the gap vanishes at a temperature T_0, given by $\kappa T_0 = 1{\cdot}14\hbar\bar{\omega}\exp(-1/F)$. An Ehrenfest (1933) second-order phase transition occurs there. The specific heat calculated from the above free energy is in fair agreement with experiment. More direct evidence for the temperature-dependent energy gap is obtained from the experiments of, e.g., Biondi *et al.* (1958 a, b), Morse and Bohm (1957), and again agrees with the theoretical prediction.

§ 4. ELECTRODYNAMIC PROPERTIES OF SUPERCONDUCTORS

4.1. *Supercurrents*

We have seen how the phenomenological energy gap model has been justified by the quasi-particle transformation. Many of the observed properties of superconductors follow in a natural way, in particular the thermal properties. The property of superconductivity itself is however more elusive. The mere existence of an energy gap in the 'individual particle' excitation spectrum is not sufficient†; indeed it is equally characteristic of insulators.

The properties most characteristic of superconductivity are the vanishing of the electrical resistance and the Meissner effect. It is here that the microscopic theory is still incomplete. The absence of resistance is partially understood; a demonstration follows that at zero temperature there is no scattering of an electric current, that is to say the residual resistance is zero. The vanishing of the ideal resistance (when $T \neq 0$) still remains unproved.

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† Bardeen (1956) has attempted to show that the Meissner effect does indeed follow from the energy-gap model with some apparently plausible additional assumptions, but Buckingham (1957) has disproved the consistency of these assumptions.

There is still no clear physical picture of how the Meissner effect arises. Mathematical derivations have been given, but Schafroth (1951, 1958) has pointed out that almost any error will lead to a spurious Meissner effect. A derivation in which *any* approximations are made can, therefore, be misleading, and great care must be taken at every stage of the calculation. So far no derivation appears wholly convincing.

It can be shown (Fröhlich 1954, Bardeen *et al.* 1957, Bogoliubov 1958 a, b) that a superconductor has stationary states with a uniform macroscopic current; these states have energy as near as we please to the ground state. The density of such states is very small, so that they have no appreciable influence on the thermal properties.

The total momentum operator

$$\mathbf{P} = \sum_{\mathbf{k}s} \hbar \mathbf{k} a_{\mathbf{k}s}{}^{+} a_{\mathbf{k}s} \qquad . \; . \; . \; . \; . \; . \; . \; . \quad (4.1)$$

commutes with the Hamiltonian (2.8) and is therefore a constant of the motion. One can therefore look for solutions of the Schrödinger equation which have a specified total momentum different from zero—their orthogonality to the ground state is assured.

In one dimension, it is easy to see that the lowest state of momentum **P** is not one with an electron and hole excited, but rather a collective excitation of the whole system. Let the whole electron system have a drift velocity v. Then relative to the electrons, the lattice modes will suffer a Doppler shift in frequency; in place of (3.2), we have

$$\left.\begin{aligned} &\{\hbar(\omega_{w_0} - w_0 v) b_{w_0}{}^{+} b_{w_0} + \mathrm{i} N_e \Omega D_{w_0} (b_{w_0}{}^{+} \overline{\exp(\mathrm{i} w_0 x)} - \mathrm{c.c.})\}\chi_{w_0} = \lambda_{+}\chi_{w_0}, \\ &\{h(\omega_{w_0} + w_0 v) b_{-w_0}{}^{+} b_{-w_0} + \mathrm{i} N_e \Omega D_{w_0} (b_{-w_0}{}^{+} \overline{\exp(-\mathrm{i} w_0 x)} - \mathrm{cc})\}\chi_{-w_0} = \lambda_{-}\chi_{-w_0}, \end{aligned}\right\} \quad . \; . \; . \; . \quad (4.2)$$

and therefore in place of (3.3)

$$\bar{b}_{\pm w_0} = \mathrm{i} N_e \Omega D_{w_0} \exp(\mp \mathrm{i} w_0 x)/\hbar(\omega_{w_0} \mp w_0 v). \qquad . \; . \quad (4.3)$$

The calculation follows as in § 3.1, and leads to a half-gap

$$\Gamma = 4\zeta_0 \exp\{(1 - v^2/s^2)3/2F\}, \qquad . \; . \; . \; . \; . \; . \quad (4.4)$$

and to a total energy

$$W_1 = W + \tfrac{1}{2} N_e \Omega (m + 3\Gamma^2/F\zeta_0 s^2) v^2 \qquad . \; . \; . \; . \; . \quad (4.5)$$

where W is the ground state energy (3.15) (Fröhlich 1954); the effective mass is macroscopic.

In a similar way, supercurrents can occur in the three-dimensional case. The method of Bogoliubov (1958 a, b) will be followed here; the momentum conservation is treated, like the particle conservation law, by introducing a Lagrangian undetermined multiplier $\mathbf{v}$. The Hamiltonian is taken to be

$$\mathscr{H} = H - \zeta \sum_{\mathbf{k},s} a_{\mathbf{k}s}{}^{+} a_{\mathbf{k}s} - \mathbf{v}.\sum_{\mathbf{k},s} \hbar\mathbf{k} a_{\mathbf{k}s}{}^{+} a_{\mathbf{k}s} \quad . \quad . \quad . \quad . \quad (4.6)$$

$$= \sum_{\mathbf{k},s} (\epsilon_{\mathbf{k}} - \zeta - \hbar\mathbf{v}\,.\,\mathbf{k}) a_{\mathbf{k}s}{}^{+} a_{\mathbf{k}s} + H_{\text{phon}} + H_{\text{int}} + H_{\text{Coulomb}}$$

$$= \sum_{\mathbf{k},s} (\epsilon_{\mathbf{k}-m\mathbf{v}} - \tfrac{1}{2}mv^2 - \zeta) a_{\mathbf{k}s}{}^{+} a_{\mathbf{k}s} + H_{\text{phon}} + H_{\text{int}} + H_{\text{Coulomb}}. \quad . \quad (4.7)$$

With the substitutions

$$\left.\begin{aligned} \mathbf{k}' &= \mathbf{k} - m\mathbf{v} \\ \zeta' &= \zeta + \tfrac{1}{2}mv^2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.8)$$

(4.7) reduces to (2.8) with the extra term $-\zeta'\mathscr{N}$. The lowest state with velocity $\mathbf{v}$ has energy $\frac{1}{2}\mathscr{N}mv^2$; the collective motion behaves like a single degree of freedom of mass $\mathscr{N}m$. Since there is still an energy gap separating such states from quasi-particle states, it follows that a supercurrent at absolute zero is metastable (cf. Landau's (1941, 1947) theory of superfluidity). It has still to be investigated whether at a finite temperature the supercurrent can lose its energy to 'individual' modes of motion. In view of its high mass, it will only give up $\sim 1/\mathscr{N}$ of its energy in a single collision, but it should be expected to have many more collisions than an individual particle. The metastability of persistent currents is equivalent to the vanishing of residual resistance, i.e. of elastic scattering of electrons by lattice defects. The still undecided question is whether the ideal resistance can also be shown to vanish. (In this connection, the experimental results of Galkin *et al.* (1957) should be mentioned—it appears that fluctuations can occur in which the resistance R approaches $10^{-4}R_n$, where R_n is the normal state value.)

4.2. *The Meissner Effect*

In §4.1, it has been shown that persistent currents can exist in superconductors (with cyclic boundary conditions) i.e. the vanishing of the resistance at zero temperature has been demonstrated. For a complete microscopic theory of superconductivity, it would still have to be shown that a magnetic field is excluded from the body—i.e. that the first of London's eqns. (1.1) (or something similar to it) holds. Unfortunately no satisfactory demonstration has yet been advanced.

It is useful to reformulate London's phenomenological theory in terms of the Fourier components $\mathbf{j}(\mathbf{k})$, $\mathbf{A}(\mathbf{k})$ of the current and vector potential (Schafroth 1951).

The general relation between current and vector potential, in an arbitrary gauge (μ, $\nu = 1$, 2, 3)

$$j_\mu(\mathbf{x}) = \sum_\nu \int d^3x' K_{\mu\nu}(\mathbf{x}-\mathbf{x}') A_\nu(\mathbf{x}') \quad . \quad . \quad . \quad . \quad (4.9)$$

becomes, in Fourier space,

$$j_\mu(\mathbf{p}) = \sum_\nu K_{\mu\nu}(\mathbf{p}) A_\nu(\mathbf{p}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.10)$$

Gauge invariance and continuity require

$$\sum_{\nu} K_{\mu\nu}p_{\nu} = \sum_{\mu} p_{\mu}K_{\mu\nu} = 0. \qquad (4.11)$$

Let us write

$$K_{\mu\nu} = \varpi_1(p^2)p_{\mu}p_{\nu} + \varpi_2(p^2)p^2\delta_{\mu\nu}. \qquad (4.12)$$

In an isotropic medium, (4.11) can be satisfied only if

$$\varpi_1 + \varpi_2 = 0 \qquad (4.13)$$

giving, from (4.10)

$$i\mathbf{p}_{\wedge}\mathbf{j}(\mathbf{p}) = -p^2\varpi_2\mathscr{H}(\mathbf{p}) \qquad (4.14)$$

where $\mathscr{H}(\mathbf{p})$ is the Fourier component of the magnetic field $\mathscr{H} = \text{curl}\,\mathbf{A}$.

If $\varpi_2(p^2)$ is regular for small p,

$$\varpi_2(p^2) = a_0 + a_1p^2 + \ldots, \qquad (4.15)$$

then (4.14) gives, in configuration space,

$$\text{curl}\,\mathbf{j} = -a_0\nabla^2\mathscr{H} - a_1\nabla^4\mathscr{H}\ldots, \qquad (4.16)$$

which is just the usual expression for the diamagnetic current (with higher order corrections for field inhomogeneity). On the other hand, a simple pole in $\varpi_2(p^2)$ gives the Meissner effect, since if

$$\varpi_2(p^2) = a_{-1}p^{-2} + a_0 + a_1p^2 + \ldots \qquad (4.17)$$

then

$$i\mathbf{p}_{\wedge}\mathbf{j}(\mathbf{p}) = -a_{-1}\mathscr{H}(\mathbf{p}) - a_0p^2\mathscr{H}(\mathbf{p})\ldots \qquad (4.18)$$

i.e.

$$\text{curl}\,\mathbf{j} = -a_{-1}\mathscr{H} + \ldots, \qquad (4.19)$$

which is London's first eqn. (1.1) (apart from higher order corrections). Hence, provided gauge-invariance is accurately preserved throughout, to decide if a model exhibits a Meissner effect, it is sufficient to show that $\varpi_2(p^2)$ has a simple pole. Violation of gauge invariance, however, can introduce just such a pole; it is therefore likely to lead to a spurious Meissner effect.

The simplified Hamiltonian of Bardeen *et al.* (3.17), (3.18) is not gauge-invariant, although Fröhlich's original Hamiltonian (2.8) is. The renormalization, if carried through exactly, cannot of course, spoil the gauge invariance. It is the simplification or 'truncation' which does so. The difficulty arises in writing down the Hamiltonian in the presence of an electromagnetic field. In the untransformed Hamiltonian, no difficulties arise, since it contains only a term quadratic in the electron momentum operator $\mathbf{p}_i = i\hbar\nabla_i$, and terms independent of $\mathbf{p}_i$, which commute with $\mathbf{x}_i$,

$$H = \sum_i p_i{}^2/2m + V(\ldots\mathbf{x}_i\ldots;\ b_{\mathbf{w}}{}^+,\ldots b_{\mathbf{w}}\ldots). \qquad (4.20)$$

Hence, in the presence of a field, we need merely to replace $\mathbf{p}$ by $\mathbf{p} - e\mathbf{A}/c$, and to write for the current density operator

$$\mathbf{j}(\mathbf{x}) = (e/2m)\sum_i\{\mathbf{p}_i\delta(\mathbf{x}_i - \mathbf{x}) + \delta(\mathbf{x}_i - \mathbf{x})\mathbf{p}_i - 2\mathbf{A}(\mathbf{x}_i)(e/c)\delta(\mathbf{x}_i - \mathbf{x})\} \quad (4.21)$$

(again obtained by replacing $\mathbf{p}$ by $\mathbf{p}-e\mathbf{A}/c$ in the expression for the current with no magnetic field).

If however, in (4.20), V is a function of the momenta too (as it is in Bardeen *et al.*), then (4.21) does not automatically hold (Schafroth 1958), since then

$$[\mathbf{x}_i, V] \neq 0. \qquad (4.22)$$

Bardeen *et al.* nevertheless assume (4.21) and Anderson (1958) has shown that this choice leads to an approximately gauge invariant expression for the current density in the ground state. That this is too weak a condition has been demonstrated by Schafroth—he shows that even if $\varpi_1(p^2)+\varpi_2(p^2)=0$ (4.13), and ϖ_1, ϖ_2 are singular, so that

$$\lim_{p\to 0} p^2\varpi_1(p^2)-p^2\varpi_2(p^2)\neq 0 \qquad (4.23)$$

(respectively the 'longitudinal' and 'transverse' sum rules of Anderson (1958)), the arbitrariness in the choice (4.21) prevents one from drawing any conclusions about a Meissner effect.

Since there is no unique procedure for defining the current operator, to the postulated current density (4.21) one may add a term

$$\mathbf{i}(\mathbf{x}) = -(\lambda/N_e\Omega)\mathbf{A}(\mathbf{x}) \qquad (4.24)$$

where λ is arbitrary, and where the only restriction on the gauge is

$$\operatorname{div}\mathbf{A}=0. \qquad (4.25)$$

In Fourier space,

$$i_\mu(\mathbf{p}) = -\lambda\sum_\nu (p_\mu p_\nu - \delta_{\mu\nu}p^2)A_\nu(p)/p^2 \qquad (4.26)$$

so that if $\mathbf{j}(\mathbf{x})$ is gauge-invariant, so is $\mathbf{j}(\mathbf{x})+\mathbf{i}(\mathbf{x})$. The addition of $\mathbf{i}$ to $\mathbf{j}$ will however alter (4.23),

$$p^2\{\varpi_1(p^2)-\varpi_2(p^2)\}\to p^2\{\varpi_1(p^2)-\varpi_2(p^2)\}-2\lambda. \qquad (4.27)$$

Since λ is arbitrary, the magnitude of the Meissner effect is arbitrary and in particular zero for a suitable choice of λ. The good agreement of the predictions of Bardeen *et al.* with experiment, for these properties of superconductors, thus appears fortuitous.

The difficulty arises, of course, because there is no unique choice for the current density operator, when the Hamiltonian is not gauge invariant. If instead of the 'truncated' Hamiltonian one used the full renormalized Hamiltonian, then the expression for the current density would be unique—it would be got by transforming (4.21), under the unitary transformation (2.29). Unfortunately one cannot find a further unitary transformation leading from (3.19) to (3.31), i.e. a transformation which would 'truncate' the interaction Hamiltonian.

A valid procedure would be, therefore, to start with the Hamiltonian (2.8), which has a unique current density (4.21) associated with it and to subject both to the Bogoliubov transformation. Attempts along these lines have been made by Rickayzen (1958) and Wentzel (1958). Rickayzen, after performing the Bogoliubov transformation, makes a non-gauge-invariant approximation, and it appears that one could introduce Schafroth's arbitrary Meissner effect (4.24) there at a later stage in the calculation than Anderson or Bardeen *et al.* Wentzel's calculation is gauge-invariant at all stages, but he does make other approximations—namely a perturbation theoretical expansion of the magnetic terms in the Hamiltonian. It is not yet clear whether this type of approximation can also lead to a spurious Meissner effect (Schafroth, private communication).

The need for a rigorously gauge-invariant formulation arises, of course, because we have not a clear physical picture of how the Meissner effect 'works'. If the programme of Schafroth *et al.* (1957) could be carried through and the condensate really shown to have the properties of a condensed ideal Bose gas, then the Meissner effect would follow *qualitatively* already. Approximations could then be safely made, without introducing a spurious Meissner effect. But in the absence of a qualitative understanding Schafroth's work shows that mathematical approximations can be very misleading.

4.3. *Paramagnetism*

The Pauli spin paramagnetism of an electron gas is masked by the Meissner diamagnetism of a superconductor, and is not directly observable by static methods. However, Reif (1957) has observed the Knight shift (i.e. the shift of the nuclear magnetic resonance frequency in the medium compared with the free atom (Knight 1949)), which gives a measure of the paramagnetic susceptibility of the electrons—Reif's experimental result is that the Knight shift in colloidal superconducting mercury is 1·6%, about 2/3 of the value (2·5%) for the normal metal. (The experimental situation is not completely clear, however. Knight *et al.* (1956) find a Knight shift of only 0·5%.)

As the theory of superconductivity stands at present, it is incapable of accounting for this Knight shift. The quasi-particle excitation spectrum with an energy gap will give zero susceptibility for fields less than $\sim 2\Gamma/\mu$ (where μ is the Bohr magneton), and therefore zero Knight shift. To account for the Knight shift, one requires the existence of excitations with small energy and with a net magnetic moment. Provided the density of such states is very small, the specific heat contribution can be small enough to preserve agreement with experiment.

Heine and Pippard (1958) have suggested that the difficulty arises from the precision of the correlations between ($\mathbf{k}, \uparrow\ ;\ -\mathbf{k}, \downarrow$) electron pairs. If, in a fairly phenomenological way, the correlation is assumed less sharp, they are able to get a Knight shift of the correct order of magnitude. However, it is just the sharpness of the correlation that endows the ground state with its 'superfluid' properties (§ 4.1). It is not obvious that the correlations can be 'smeared out' in a consistent way.

In conclusion, it appears that the nature of the 'condensation' is now well understood, arising from the electron–phonon interaction. All properties which depend mainly on the density of states or energy gap follow from the theory, and agreement between theoretical prediction and experiment leaves little to be desired. Thus e.g. the specific heat, thermal conductivity and threshold magnetic field agree well (the latter is not primarily an electromagnetic property, since it is derived from *energetic* considerations—$H_c^2/8\pi$ is equated to the 'condensation' energy per unit volume).

The electromagnetic properties are less well understood: although the ground state has been shown to have *some* 'superfluid' properties (§ 4.1), the Meissner effect has not been demonstrated in a wholly convincing way, nor the Knight shift. There is not a sufficiently clear physical picture of the process to give one confidence in the approximations, particularly as the subject has a long history of spurious Meissner effects arising from approximations.

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The Modern Theory of Superconductivity

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§ 1. INTRODUCTION

THE phenomenon of superconductivity was discovered by Kamerling-Onnes in 1911. Since then, the subject has been studied intensively during nearly fifty years and a considerable amount of experimental data has been amassed. However, this has not led to any material progress in the understanding of the physical principles underlying the phenomenon. The first step on the road to its understanding was made in connection with the discovery of superfluidity and the construction of a theory for it (Landau 1941). Landau also drew attention to the analogy between superfluidity and superconductivity, which allows superconductivity to be considered as the superfluidity of the electron gas in the metal.

The second important step was the discovery (Allen *et al.* 1950 a) of the isotope effect, i.e. the dependence of the critical temperature T_c on the isotopic mass of the superconductor. This effect directly showed the importance of the lattice in the phenomenon of superconductivity and in this connection Fröhlich (1950) and Bardeen (1950) pointed out the possibility of a new type of interaction between electrons by the exchange of phonons. However, until very recently this approach did not give satisfactory results and the cause of superconductivity remained essentially unknown. On the other hand, it was clear to all (Feynman 1957) that there were sufficient experimental data to construct a theory and that all that was lacking was some fundamental idea which would enable the orthodox methods of quantum mechanics to explain the whole phenomenon.

This missing idea is contained in a short letter by Cooper (1956). Cooper showed that for a pair of particles which obey Fermi statistics and which have a mutual attraction, no matter how weak, there will exist a bound state. This extremely important result is the key to the understanding of the phenomenon of superconductivity. In the ground state of a metal without taking account of the Cooper effect the electrons fill (in the isotropic case) the Fermi sphere in momentum space. If however we assume that there is in metals an effective attraction between the electrons, pairing will occur and the ground state will then be lower than for free electrons by the binding energy of these pairs. The electron pairs have integral spin and therefore obey Bose statistics. Now it is known that a Bose gas is superfluid at absolute zero and applied to a Bose gas of charged particles this property manifests itself as superconductivity. The above considerations do not pretend to be rigorous but they do indicate that superconductivity can be completely explained on the basis of the Cooper effect.

A complete and consistent theory of superconductivity was given by Bardeen *et al.* (1957, referred to here as BCS 1957). They put forward a technique which enabled them to examine the ground state of a superconductor (i.e. that at $T=0$) and to obtain the excitation spectrum. On this basis they calculated the thermodynamic properties and deduced the electrodynamic equations for superconductors in weak fields. In the field of thermodynamics the fact that a finite jump is obtained in the specific heat at the transition between the normal and superconducting states deserves mention. For the description of the behaviour of superconductors in a magnetic field, a quantity characterizing the size of the electron pair turned out to be an important parameter. If the penetration depth of the field is large compared to this parameter, there is a local relation between the current and the field potential and the old London equations are then valid. If however the penetration depth is small compared to the above parameter, there is no local relation between the current and the potential and the properties of the superconductor are then described by other equations, obtained earlier by Pippard (1953) on semi-intuitive grounds.

Bogolyubov (1958, see also Bogolyubov *et al.* 1958) put forward several original methods which lead to the results of BCS (1957), and one of these is very similar to the technique used by BCS. Another, which seems to us more natural, is similar to the method which he used in the study of the excitation spectrum of a Bose gas.

The authors of the present article, using Bogolyubov's technique, have carried out calculations analogous to those of BCS (1957), and an exposition of the modern theory of superconductivity is given on the basis of the Cooper effect and the above approach. Some results are also given which are not contained in the work of BCS. In particular the rôle of the electronic Coulomb interaction was not explained by these authors. It should be pointed out that that there is as yet no rigorous solution to this problem, though there is an interesting paper by Tolmachev, (see Bogolyubov *et al.* 1958) which showed that the effect of Coulomb repulsion is weakened in the presence of electronic interaction through a phonon field. The results obtained by L. P. Gor'kov and the authors of the present article on the behaviour of superconductors in high frequency electromagnetic fields are also given on the basis of the new theory (Abrikosov *et al.* 1958).

§ 2. The Cooper Effect

To understand the basic content of Cooper's idea, we consider the following example: a gas of Fermi particles with a direct interaction between particles with energies $\epsilon(k)$ within a small energy range ω in the neighbourhood of the Fermi sphere $-\omega \leqslant \epsilon(k)-\epsilon(k_1) \leqslant \omega$ and constant inside this region† (Abrikosov and Khalatnikov 1957). The Hamiltonian of such an interaction will be of the form:

$$H' = g\sum a^{+}(k_1', \tfrac{1}{2})a^{+}(k_2', -\tfrac{1}{2})a(k_2, \tfrac{1}{2})a(k_2, -\tfrac{1}{2}) \quad (|\xi(k)| \leqslant \omega). \qquad (2.1)$$

where the summation is over values of $\mathbf{k}_1$ etc. such that

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2'.$$

The operators $a^{+}(k, \sigma)$ and $a(k, \sigma)$ correspond to the creation and annihilation of particles with given momentum and direction of spin; $\xi(k)$ is the energy of the particle, reckoned from the Fermi surface, and the summation in (2.1) is made with due account of conservation of momentum. We shall assume that the constant g is small enough to permit the application of perturbation theory.

We consider the scattering of two particles with nearly opposite momenta, i.e. such that $|\mathbf{k}_1 + \mathbf{k}_2| \ll k_0$. To a first approximation the scattering amplitude is simply equal to g if the particles have opposite spins and zero if the spins are parallel. This is of course also true for an arbitrary angle between $\mathbf{k}_1$ and $\mathbf{k}_2$, but the next approximation already shows the singularity of the case examined. Although the second approximation gives only a small correction to the scattering amplitude for an arbitrary angle between $\mathbf{k}_1$ and $\mathbf{k}_2$, the correction may increase without limit for almost opposite momenta. Thus let us consider the terms of the transition amplitude corresponding to the transition of two particles outside the Fermi sphere ($\xi(k) > 0$) without participation of the particles inside the Fermi sphere. Such a term arises only for particles of opposite spins and takes the form (setting $\hbar = 1$ in this and subsequent formulae)

$$-\frac{g^2}{(2\pi)^3}\int d^3q \frac{1}{\xi(k_1) + \xi(k_2) - \xi(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{q}) - \xi(q)} \quad . \quad . \quad (2.2)$$

where the integration is in the regions

$$0 < \xi(q) < \omega, \quad 0 < \xi(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{q}) < \omega.$$

In this formula, since all the momenta k are near to k_0, we may put $\xi(k) = v(k - k_0)$, v being the velocity of a particle at the Fermi surface. If we also introduce the notation $\lambda = \xi_1 + \xi_2$ and $\mu = v|\mathbf{k}_1 + \mathbf{k}_2|$, then since λ and μ are small we get

$$-\frac{2\pi g^2 k_0^2}{(2\pi^3)v}\int_0^{\omega} d\xi(q)\int_{-1}^{1} d(\cos\theta)\frac{1}{\lambda + \mu\cos\theta - 2\xi(q)}. \quad . \quad . \quad (2.3)$$

This integral is logarithmic in $\xi(q)$. For the case $\lambda \ll \omega$ and $\mu \ll \omega$ it is not difficult to see that to the first order this expression is equal to

$$\frac{g^2 K_0^2}{4\pi^2 v}\ln\frac{2\omega}{\max\{\lambda, \mu\}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.4)$$

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† Later we shall see the relation between this and the real interaction between electrons in a metal.

It is easy to see that such a quantity contains a term which corresponds to a transition of two other particles which are inside the Fermi surface to a final state $\mathbf{k}_1'\mathbf{k}_2'$ and the subsequent transition of the initial particles to the positions thus made vacant. If we consider transitions which concern one of the initial or final particles and one of the particles from the Fermi surface the logarithmic factor is absent. (Only this type of virtual transition may take place for parallel spins.)

Consequently, with an accuracy including small terms, the scattering amplitude for particles with antiparallel spins and almost opposite momenta is to the second order of the form

$$A^{(2)} \to g + \frac{g^2 k_0^2}{2\pi^2 v} \ln \frac{2\omega}{\max\{\lambda, \mu\}}. \qquad (2.5)$$

This expression is however, not correct when μ and λ are very small, in which case the second term of formula (2.5) may become larger than the first, and higher terms of the series given by perturbation theory must be included. In this it is sufficient to limit ourselves to those which for each power of g contain the corresponding power of the large logarithm. It is easy to see that these terms arise for such virtual processes in which the initial pair is not broken up, i.e. both particles simultaneously transform either inside or outside the Fermi surface. The series which arises as a result of this is a geometric progression, the first two terms of which are given by formula (2.5). The sum of the whole series is evidently

$$A = g \Big/ \left[1 - \frac{g k_0^2}{2\pi^2 v} \ln \frac{2\omega}{\max\{\mu, \lambda\}}\right]. \qquad (2.6)$$

In the Hamiltonian H' the constant g can be either negative or positive. In the first case (repulsion) the scattering amplitude tends to zero for small λ and μ. However, in the second case (attraction) the position is completely different and in fact, for sufficiently small λ and μ the scattering amplitude has a pole, which corresponds to the appearance of a bound state. We note that the formation of such a state would not be possible without the presence of the other particles, which, together with those considered, are in the ground state and form the Fermi sphere. The quantity λ corresponds to the binding energy of this state. Different values of λ will correspond to different values of μ, i.e. different angles between $\mathbf{k}_1$ and $\mathbf{k}_2$, but the calculation of the dependence is beyond the limits of our accuracy. From considerations of symmetry it is natural to conclude that the ground state is that in which $\mathbf{k}_1$ and $\mathbf{k}_2$ are opposite. In this case the value of λ corresponding to the pole (denoted by Δ_0) will be equal to

$$\Delta_0 = 2\omega \exp\left\{-\frac{2\pi^2 v}{g k_0^2}\right\}. \qquad (2.7)$$

Thus we arrive at the conclusion that for any attraction between the particles in a Fermi gas, no matter how small, there will arise bound states of pairs of particles with opposite momenta and spins. This is the essence of the so-called Cooper phenomenon. Cooper himself obtained it by different and simplified arguments which, it should be noted, lead to quantitatively incorrect results since they do not take into account virtual transitions of the initial pair with other particles of the Fermi sphere (the second of the processes examined here).

§ 3. THE GROUND STATE OF SUPERCONDUCTORS

The existence of the isotope effect in superconductors is evidence for the important rôle played by the lattice in this phenomenon. The influence of the lattice shows itself in an electronic interaction through the phonon field and this interaction has the form of an attraction; at the same time there is also the Coulomb repulsion between the electrons. The electronic interaction through the phonon field can be described using the Fröhlich Hamiltonian, though a consistent account of the Coulomb interaction is as yet an unsolved problem. The difficulty in taking account of the Coulomb interaction may be avoided by the introduction of a certain effective direct interaction between the electrons. We will consider that this direct four-fermion interaction leads to a certain effective attraction, which is represented by a small binding constant g. Such an attraction only acts in the electrons in the neighbourhood of the Fermi surface, in a certain narrow momentum range the width of which is of the order of the maximum Debye frequency. If there were no Coulomb interaction this could be considered rigorous, since the phonon interaction concerns only electrons in this momentum band†.

A direct four-fermion interaction is described by the Bardeen Hamiltonian

$$H=\sum_{k\sigma}\left(\frac{k^2}{2m}-\mu\right)a^+(k,\sigma)a(k,\sigma)$$

$$+g\sum a^+(k_1',\tfrac{1}{2})a^+(k_1',-\tfrac{1}{2})a(k_1,\tfrac{1}{2})a(k_2-\tfrac{1}{2}) \quad . \quad . \quad . \quad . \quad (3.1)$$

where the second summation is over values

$$\mathbf{k}_1-\mathbf{k}_2'=\mathbf{k}_2'-\mathbf{k}_2\neq 0,$$

and where $\mu=k_0{}^2/2m$ and k_0 is the momentum at the Fermi surface. In order that in further calculations we should not need to consider conservation of the number of particles in the system, the term

$$-\mu N=-\mu\sum a^+(k,\sigma)a(k,\sigma)$$

has been induced in the Hamiltonian (3.1). The difference

$$k^2/2m-\mu=v(k-k_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.2)$$

(for values of k near to k_0) will in future be denoted by the letter ξ_k. The condition for the momenta in the second sum in (3.1) is due to the fact that, as the energy of the phonon tends to zero, so does the phonon interaction. Instead of the operators $a^+(k,\sigma)$, $a(k,\sigma)$ we introduce new ones

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† The Coulomb interaction will be dealt with in more detail below.

$\alpha(k,0)$, $\alpha(k,1)$ and defined by the equations

$$\left.\begin{aligned} a(k,\tfrac{1}{2}) &= u_k\alpha(k,1)+v_k\alpha^+(-k,0) \\ a(k,-\tfrac{1}{2}) &= u_k\alpha(k,0)-v_k\alpha^+(-k,0) \end{aligned}\right\} \qquad (3.3)$$

where u_k and v_k satisfy the condition

$$u_k^2+v_k^2=1. \qquad (3.4)$$

When these conditions are obeyed the commutation relation for the new operators $\alpha(k)$ will be the same as that for the previous ones $a(k)$. According to Cooper (1956) the Hamiltonian (3.1) led to the possibility of the formation of bound electrons. The operators $\alpha(k)$ characterize the reconstructed system in which electron pairing has taken place. In the ground state of the new system the creation of pairs with opposite momenta and spins must be forbidden, although this was possible in the original system. Therefore in the Hamiltonian (3.1) we express the operators $a(k)$ in terms of $\alpha(k)$ and obtain the conditions which forbid the creation of pairs of excitations $\alpha(k,1)$ and $\alpha(-k,0)$. Hence the Hamiltonian (3.1) acquires the following form

$$H=H_0+H_1+H_2$$

where

$$\begin{aligned} H_0 &= 2\sum_k \xi_k v_k^2+\sum_k (u_k^2-v_k^2)\{\alpha^+(k,1)\alpha(k,1)+\alpha^+(k,0)\alpha(k,0)\}, \\ H_1 &= 2\sum_k \xi_k u_k v_k\{\alpha^+(k,1)\alpha^+(-k,0)+\alpha(-k,0)\alpha(k,1)\}, \\ H_2 &= g\sum\{u(k_1')u(k_2')\alpha^+(k_1',1)\alpha^+(k_2',0)-v(k_1')v(k_2') \\ &\quad \times\alpha(-k_1',0)\alpha(-k_2',1)-u(k_1')v(k_2')\alpha^+(k_1',1)\alpha(-k_2',1) \\ &\quad +v(k_2')u(k_2')\alpha(-k_1',0)\alpha^+(k_2',0)\}\{u(k_1)u(k_2)\alpha(k_1,0)\alpha(k_2,0) \\ &\quad -v(k_1)v(k_2)\alpha^+(-k_1,1)\alpha^+(-k_2,1)-u(k_1)v(k_2)\alpha(k_1,1)\alpha^+(-k_2,1) \\ &\quad +v(k_1)u(k_2)\alpha^+(-k_1,0)\alpha(k_2,0)\}. \qquad (3.5) \end{aligned}$$

Here $u(k)$ is written for u_k and the summation in H_2 is over

$$\mathbf{k}_1-\mathbf{k}_1'=\mathbf{k}_2'-\mathbf{k}_2\neq 0.$$

Let us now consider a superconductor at a $T=0$ and let us calculate the properties of the system in the ground state. The operator $\alpha^+(k)$, acting on a vacuum, will create a quasi-particle, but the action of the operator $\alpha(k)$ on a vacuum gives zero, since at $T=0$ all the states are full. The condition forbidding the creation of pairs is obtained by equating to zero the coefficients of all the terms which contain the product of the two operators $\alpha^+(k_1)$, $\alpha^+(-k_0)$. Thus we get

$$2\xi_k u_k v_k = g(u_k^2-v_k^2)\sum_{k'} u_{k'}v_{k'}. \qquad (3.6)$$

We introduce the notation

$$\Delta(0)=g\sum_k u_k v_k, \qquad (3.7)$$

and substituting for u_k and v_k in (3.6) and (3.7) in terms of ξ_k and $\Delta(0)$, we have

$$u_k^2=\tfrac{1}{2}[1+\xi_k/\sqrt{\{\Delta(0)^2+\xi_k^2\}}], \qquad (3.8)$$

$$v_k^2=\tfrac{1}{2}[1-\xi_k/\sqrt{\{\Delta(0)^2+\xi_k^2\}}]. \qquad (3.9)$$

Substituting these expressions for u_k and v_k in (3.6) we obtain an equation which defines the constant Δ, namely

$$1=\tfrac{1}{2}g\sum_{-\omega}^{\omega}1/\sqrt{\{\Delta(0)^2+\xi_k{}^2\}}. \qquad (3.10)$$

After transforming the sum in (3.10) to an integral and integrating we get

$$1=\tfrac{1}{2}g\nu\ln\{2\omega/\Delta(0)\} \qquad (3.11)$$

where $\nu=k_0{}^2/\pi^2 v$ and (3.11) defines the constant $\Delta(0)$. As we shall see below the constant $\Delta(0)$ plays the part of an energy gap in the spectrum of excitations; from (3.11) its magnitude is

$$D(0)=2\omega\exp(-2/g\nu) \qquad (3.12)$$

which is the same as Cooper's binding energy (2.7) of an electron pair. From the form of the expression it is easily seen that no perturbation theory could produce this effect, since the function $\exp(-1/x)$ cannot be expanded in a power series in the neighbourhood of $x=0$.

The energy of the ground state is obtained by the diagonalization of the Hamiltonian (3.5)

$$E_0=2\sum_{k}\xi_k v_k{}^2-g\sum_{k,k_1}u_k v_k u_{k_1}v_{k_1}. \qquad (3.13)$$

Varying this expression with respect to n and subject to the supplementary condition (3.4) we obtain (3.6) as an extremum condition. Thus equation (3.6) is simultaneously both the condition forbidding the creation of pairs and the condition for an extremum of the energy.

Using eqns. (3.8) and (3.9) for u_k and v_k we write the energy of the ground state in the form

$$E_0=2\sum_{\xi<0}\xi_k-\tfrac{1}{2}\Delta(0)^2\sum_{k}1/\sqrt{\{\Delta(0)^2+\xi_k{}^2\}}. \qquad (3.14)$$

The first summation is taken only over negative ξ_k (inside the Fermi surface), since v_k tends to 0 very quickly outside the Fermi sphere ($\xi_k>0$). From formula (3.14) we see that because of the second negative term the energy obtained for the ground state is lower than the zero-point energy corresponding to a full Fermi sphere for free electrons. We note that (3.11) has a solution only for $g>0$, i.e. for an attraction between the particles.

3.1. *The Rôle of the Coulomb Interaction between Electrons*
(*Bogolyubov et al.* 1958)

In order that superconductivity should be possible it is necessary that the total effect of the phonon and Coulomb interactions should be attractive, leading to the formation of electron pairs; we shall therefore consider the rôle of the Coulomb interaction in more detail. Since the problem of an exact treatment of the Coulomb interaction has not yet been solved, we shall try to take account of it by means of a mode (Abrikosov *et al.* 1958).

The Hamiltonian of the initial system previously included a certain effective attraction which was effective in the momentum range $-\omega$ to ω, where ω corresponds to the limiting Debye frequency of the lattice. This interaction model was equivalent to an interaction through phonons. The Coulomb interaction can also be accounted for approximately by a model if the Hamiltonian includes a constant repulsive interaction which acts over the momentum range $-\omega_1$ to ω_1, which is larger than the first range†. Thus the initial Hamiltonian now has the form:

$$H=\sum_k a^+(k,\sigma)\,a(k,\sigma)+\sum_{k,k_1} g(k,k_1)\,a^+(k,\tfrac{1}{2})\,a^+(k_1,-\tfrac{1}{2})\,a(k,\tfrac{1}{2})\,a\,(k_1,-\tfrac{1}{2})$$

where

$$g(k,k_1)=\begin{cases} g+g_1, & |\xi(\mathbf{k})|,\,|\xi(\mathbf{k}_1)|<\omega \\ \quad g_1, & |\xi(\mathbf{k})|,\,|\xi(\mathbf{k}_1)|<\omega \end{cases} \qquad . \quad . \quad . \quad . \quad (3.15)$$

and

$$g>0,\ g_1<0.$$

The further calculations are carried out as before, i.e. the operators $\alpha(k,1)$ and $\alpha(k,0)$ are introduced as in (3.3). The Hamiltonian (3.15) is diagonalized and the transformation coefficients u_k and v_k are found from the condition for an energy minimum. We then find

$$u_k{}^2=\tfrac{1}{2}\,[1+\xi_k/\surd(\xi_k{}^2+\Delta_k{}^2)], \qquad . \quad . \quad . \quad . \quad . \quad (3.16)$$

$$v_k{}^2=\tfrac{1}{2}\,[1-\xi_k/\surd(\xi_k{}^2+\Delta_k{}^2)]. \qquad . \quad . \quad . \quad . \quad . \quad (3.17)$$

The quantity Δ_k is now a function of k, defined by the equation

$$\Delta_k=\sum_{k_1} g(k,k_1)\,u_{k_1}v_{k_1}. \qquad . \quad . \quad . \quad . \quad . \quad (3.18)$$

Using this equation we get two equations which define the quantity Δ in the two regions of momentum space:

$$\Delta_k=\begin{cases}\Delta_0 & |\xi(k)|<\omega, \\ \Delta_1 & \omega<|\xi(k)|<\omega_1,\end{cases}$$

$$\Delta_0=\tfrac{1}{2}(g+g_1)\,\Delta_0\ln\,(2\omega/\Delta_0)+\tfrac{1}{2}g_1\,\Delta_1\ln\,(\omega_1/\omega),$$

$$\Delta_1=\tfrac{1}{2}g_1\,\Delta_0\ln\,(2\omega/\Delta_0)+\tfrac{1}{2}g_1\,\Delta_1\ln\,(\omega_1/\omega). \qquad . \quad . \quad . \quad (3.19)$$

Eliminating Δ_1 from these equations we get an equation for Δ_0:

$$\tfrac{1}{2}\ln\,(2\omega/\Delta_0)\left[g+\frac{g_1}{1-\tfrac{1}{2}g_1\ln\,(\omega_1/\omega)}\right]=1. \qquad . \quad . \quad . \quad (3.20)$$

This equation has a solution only when the terms in the square brackets exceed unity and this condition is the criterion for the possibility of a bound state, and consequently for the occurrence of superconductivity. It is interesting that the interaction $g(k,k_1)$ may be repulsive over the whole momentum region $(g+g_1<0)$ but that nevertheless the condition for superconductivity may be satisfied. This is related to the fact that the Coulomb interaction which acts over a wider momentum range is renormalized, and the renormalization contains the large logarithm $\ln\,(\omega_1/\omega)$.

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† This corresponds to the fact that the Coulomb interaction is screened at distances of the order of the lattice spacing.

§ 4. THE THERMODYNAMICS OF SUPERCONDUCTORS

We will now examine the properties of superconductors at temperatures other than the absolute zero. At non-zero temperatures systems of electrons are not in the ground state, and consequently the average values of the operator products will no longer be zero (as for $T=0$), but will equal the corresponding occupation numbers n_k.

We define the operators u_k and v_k analogously to the previous case, so that in the Hamiltonian all terms which lead to the creation of pairs should cancel out and the corresponding condition has the form:

$$2\xi_k u_k v_k = g(u_k^2 - v_k^2) \sum_{k'} u_{k'} v_{k'} (1 - n_{k'1} - n_{k'0}). \quad . \quad . \quad (4.1)$$

Introducing the notation

$$\Delta = g \sum u_k v_k (1 - n_{k1} - n_{k0}), \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

we express u_k and v_k in terms of ξ_k and Δ and obtain the following expression for Δ:

$$1 = \tfrac{1}{2} g \sum (1 - n_{k1} - n_{k0}) / \sqrt{(\Delta^2 + \xi_k^2)}. \quad . \quad . \quad . \quad . \quad (4.4)$$

For u_k and v_k we use the earlier formulae (3.8), (3.9):

$$u_k^2 \text{ or } v_k^2 = \tfrac{1}{2}\{1 \pm \xi_k / \sqrt{(\Delta^2 + \xi_k^2)}\}. \quad . \quad . \quad . \quad . \quad (4.5)$$

We now calculate the energy of the system in the excited state as a function of the distribution of excitations. Taking the diagonal matrix element of the Hamiltonian (3.5) we get

$$E = 2 \sum_k \xi_k v_k^2 + \sum_k \xi_k (u_k^2 - v_k^2)(n_{k1} + n_{k0})$$
$$- g \sum_{kk'} u_k v_k u_{k'} v_{k'} (1 - n_{k1} - n_{k0})(1 - n_{k'1} - n_{k'0}). \quad . \quad . \quad (4.6)$$

The system of excitations can also be considered as a system of quasi-independent particles, so that we may use the well-known formula for the entropy:

$$S = -\sum_k [n_{k0} \ln n_{k0} + (1 - n_{k0}) \ln (1 - n_{k0}) + n_{k1} \ln n_{k1} + (1 - n_{k1}) \ln (1 - n_{k1})]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.7)$$

From the condition for an extremum of the entropy for a given energy we may derive, by a method analogous to that used in the theory of a Fermi liquid by Landau (1956), the distribution functions n_{k1} and n_{k0}. They turn out to be the Fermi function

$$n_k = 1 / \{\exp[\epsilon(k)/T] + 1\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.8)$$

where $\epsilon(k)$ is the derivative of the function

$$\epsilon(k) = \delta E / \delta n_k. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.9)$$

The variation of the energy E with respect to n_k may be carried out at constant u_k and v_k. The fact is that the condition (4.4) may be derived from (4.6) as a condition for an extremum of the energy with respect to u_k; then, varying E with respect to u_k and using the condition $u_k^2 + v_k^2 = 1$, we easily obtain

$$\frac{\delta E}{\delta u_k} = -\frac{2}{v_k} \{2\xi_k u_k v_k - (u_k^2 - v_k^2)(1 - n_{k1} - n_{k0}) g \sum_{k'} u_{k'} v_{k'} (1 - n_{k'1} - n_{k'2})\} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.10)$$

which evidently coincides with (4.1). Taking this into account, we find for the excitation energy $\epsilon(k)$:

$$\epsilon(k)=\frac{\delta\epsilon}{\delta n_k}=\xi_k(u_k{}^2-v_k{}^2)+2u_k v_k g\sum_{k'}u_{k'}v_{k'}(1-n_{k'0}-n_{k'1}) \quad . \quad (4.11)$$

and from (4.1) and the (4.5) we finally obtain

$$\epsilon(k)=\sqrt{(\Delta^2+\xi_k{}^2)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.12)$$

In form this is similar to the excitation energy at $T=0$, but it must not be forgotten that the quantity Δ, which plays the rôle of an energy gap, depends on the temperature and is given by eqn. (4.4). Substituting (4.8) in (4.4) we get a relation which determines the magnitude of the energy gap:

$$\tfrac{1}{2}g\sum_k\{\tanh(\epsilon/2T)/\epsilon\}=1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.13)$$

4.1. *The Temperature Variation of the Energy Gap*

We now consider eqn. (4.13) in more detail. For $T=0$ the tanh tends to unity and integrating then with respect to $d\xi$ between the limits $-\omega$ and ω we get

$$\tfrac{1}{2}g\nu\ln(2\omega/\Delta_0)=1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.14)$$

where $\nu=k_0{}^2/\pi^2 v$. This is the condition (3.11), which was obtained earlier as determining Δ_0. Equation (4.13) can now be written as

$$\ln(2\omega/\Delta_0)=\int_\Delta^\omega\frac{\tanh(\epsilon/2kT)}{\sqrt{(\epsilon^2-\Delta^2)}}d\epsilon=\ln\frac{2\omega}{\Delta}+\int_\Delta^\omega\frac{\tanh(\epsilon/2kT)-1}{(\sqrt{\epsilon^1-\Delta^2})}d\epsilon. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.15)$$

In the last integral the upper limit may be replaced by ∞. Introducing a new variable by the substitution $\epsilon=\Delta\cosh\phi$ we get

$$\ln\frac{\Delta_0}{\Delta}=2\int_\Delta^\infty\frac{d\phi}{\exp(\Delta\cosh\phi/T)+1}. \quad . \quad . \quad . \quad . \quad . \quad (4.16)$$

From this formula we may find Δ over the whole temperature range. To do this it is convenient to express the right-hand side as a series of Bessel functions k_0.

$$\ln\left(\frac{\Delta_0}{\Delta}\right)=2\sum_{m=1}^{\infty}(-1)^{m+1}k_0\left(\frac{\Delta m}{T}\right). \quad . \quad . \quad . \quad . \quad . \quad (4.17)$$

Near $T=0$ we may take just the first term of this series and use the asymptotic expansion of the function k_0. This gives

$$\Delta=\Delta_0-\sqrt{(2\pi T\Delta_0)}\exp(-\Delta_0/T). \quad . \quad . \quad . \quad . \quad (4.18)$$

The transition to the normal state corresponds to the vanishing of Δ and therefore (4.15) may be used to find a relation between Δ_0 and the transition temperature T_c. For small values of Δ/T it is convenient to use the formula for the summation of the series (4.17):

$$\ln\frac{\Delta_0}{\Delta}=\ln\frac{\pi T}{\gamma\Delta}+2\pi\sum_{l=1}^{\infty}\left[\frac{1}{(2l-1)\pi}-\frac{1}{\sqrt{\{(\Delta/T)^2+(2l-1)^2\pi^2\}}}\right] \quad . \quad (4.19)$$

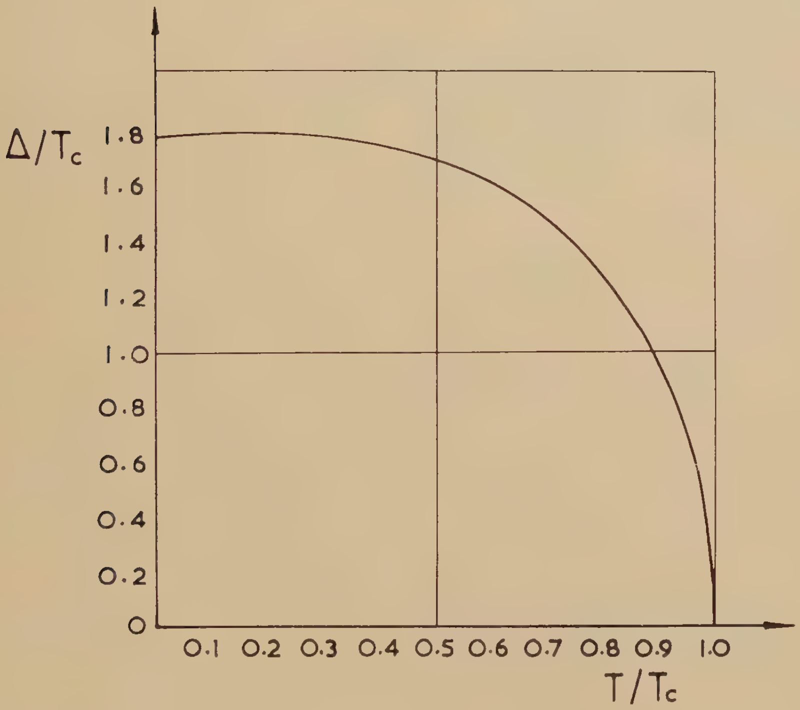
where $\ln \gamma$ is the Euler constant 0·577. Hence at the transition point we have

$$\Delta_0/T_c = \pi/\gamma = 1{\cdot}76. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.20)$$

Expanding (4.19) in powers of Δ/T, we find

$$\ln(T/T_c) = -\frac{7}{8\pi^2}\zeta(3)\left(\frac{\Delta}{T}\right)^2 T \frac{93\zeta(5)}{128\pi^4}\left(\frac{\Delta}{T}\right)^4. \quad . \quad . \quad . \qquad (4.21)$$

Fig. 1



To the first order in $(T - T_c)$

$$\Delta/T_c = 3{\cdot}06\,(1 - T/T_c)^{1/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4.22)$$

The function $\Delta(T)$ may then be calculated in detail from (4.21) and (4.19) and is shown graphically in fig. 1.

In (4.14) the coefficient ω is of the order of the maximum Debye frequency, which is inversely proportional to the square root of the atomic weight (M). Thus the energy gap in the excitation spectrum is inversely proportional to $\sqrt{M}$, and since the energy gap differs from the transition temperature only by a constant factor we therefore have

$$T \sim 1/\sqrt{M},$$

i.e. the transition temperature T_c is inversely proportional to the square root of the atomic mass (isotope effect). We note also a possible relation between the energy gap and the Debye temperature, namely, as follows from (4.14):

$$\Delta_0/\omega = 2\exp(-2/g\nu).$$

An investigation of the stability of the lattice (Tiablikov and Tolmachev 1958) leads to a criterion which limits the exponential by the following inequality:

$$2/g\nu > 2.$$

Thus the energy gap must be about an order of magnitude smaller than the Debye temperature.

4.2. *The Specific Heat*

We begin with a calculation of the entropy. From (4.7), on integration by parts and the use of (4.8), we find:

$$S = -\frac{2\nu}{T}\int_{\Delta}^{\infty} \sqrt{(\epsilon^2-\Delta^2)}\,\epsilon\frac{\partial n}{\partial \epsilon}\,d\epsilon, \quad \ldots\ldots \quad (4.23)$$

and substituting $\epsilon = \Delta \cosh\phi$ this becomes

$$S = \frac{2\Delta^2\nu}{T}\sum_{m=1}^{\infty}(-1)^{m+1}K_2\left(\frac{\Delta}{T}m\right). \quad \ldots\ldots \quad (4.24)$$

For $T = 0$ we get the asymptotic value:

$$S = \sqrt{(2\pi\Delta_0{}^3/T)}\,\nu\exp(-\Delta_0/T). \quad \ldots\ldots \quad (4.25)$$

Near the transition point T_c the expansion of formula (4.23) leads to

$$\left.\begin{aligned} S &= \frac{\pi^3}{3}T\nu\left[1-\frac{3}{2\pi^2}\left(\frac{\Delta}{T}\right)^2+\frac{3q}{8\pi^2}\left(\frac{\Delta}{T}\right)^4\right] \\ \text{where}\qquad & \\ q &= \tfrac{1}{2}\int_0^{\infty} x^{-2}\tanh^2 x\,dx \simeq 0{\cdot}8. \end{aligned}\right\} \quad \ldots \quad (4.26)$$

To calculate the specific heat, we differentiate (4.25) and, using the expansion (4.21), we find:

$$C_s(T)/C_n(T) = 2{\cdot}4 + 7{\cdot}3\,(T-T_c)/T_c. \quad \ldots\ldots \quad (4.27)$$

Here we have expressed the specific heat in terms of the value for the normal state at $T = T_c$, equal to $C_n(T_c) = \frac{1}{3}\pi^2/\nu\,T_c$. From (4.27) it follows that at $T = T_c$ the specific heat has a finite jump and that its derivative to the left of this point remains finite. A more detailed analysis shows that the next term in the expansion in $T - T_c$ is proportional to $(T_c - T)^{3/2}$.

Differentiating (4.25), we obtain an asymptotic expression for the specific heat for $T \to 0$

$$C_s(T)/C_n(T_c) = \frac{3}{\gamma}\sqrt{\frac{2}{\pi}}\left(\frac{\Delta_0}{T}\right)^{3/2}\exp\left(-\frac{\Delta_0}{T}\right). \quad \ldots \quad (4.28)$$

The full curve for the specific heat is shown in fig. 2.

In spite of the fact that the model considered, which neglects anisotropy, is a fairly rough approximation, it is interesting to compare the theoretical results obtained with the experimental data for a number of superconductors, as is done in fig. 3. The data for Sn, Zn and Al were obtained by

Zavaritskii (1958), and those for V and Nb are taken from Corak *et al.* (1956). From this diagram it is clear that in most cases the experimental data are

Fig. 2

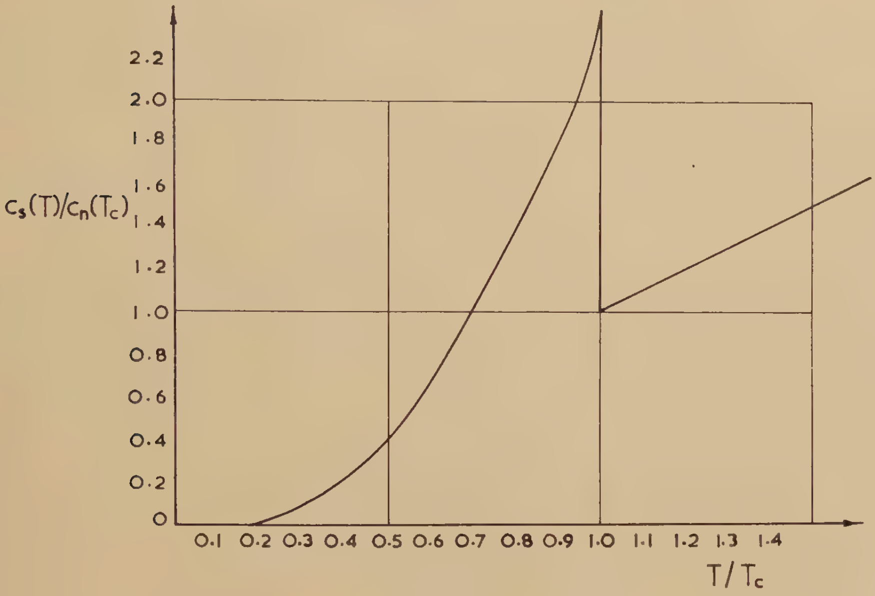
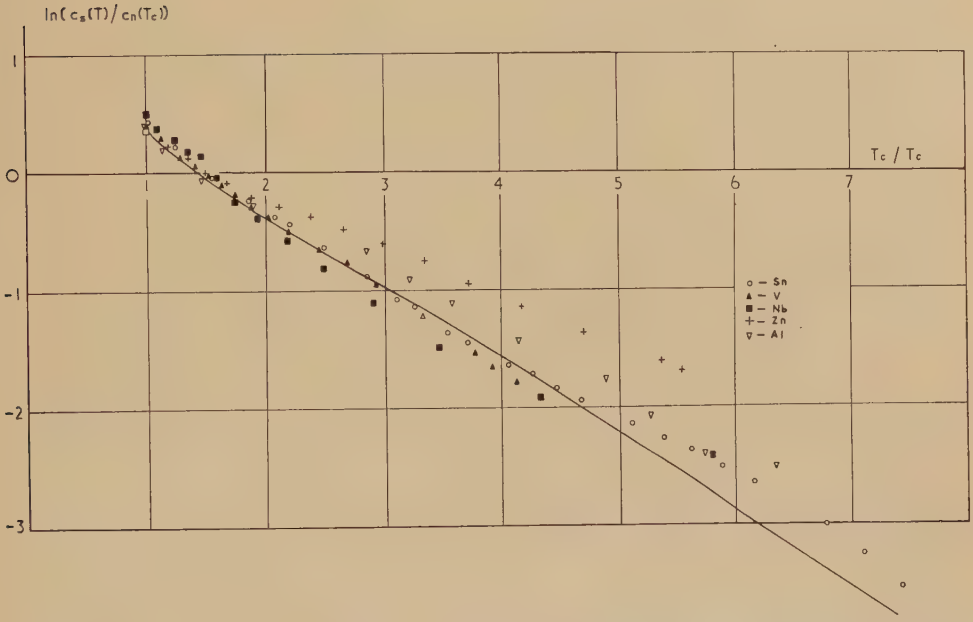


Fig. 3



quite well fitted by the theory. The worst fit is for zinc in the low temperature region, and this could be due to the fact that in this region the specific heat is very sensitive to the value of Δ_0. Since the magnitude of the jump in the specific heat does not show up well on the logarithmic scale; we give the experimental values of $C_s(T_c)/C_n(T_c)$ separately in the table.

Element	$C_s(T_c)/C_n(T_c)$
Sn	2·82
Al	2·5
Zn	2·32
V	2·52
Nb	3·07

It is evident that, despite the reasonable roughness of the model, the values which it predicts agree quite well with the experimental data.

Here it is apposite to note a characteristic peculiarity of the real anisotropic case, in which the energy gap will in general depend on direction; however at T_c the separation must tend to zero simultaneously for all directions. In the measurement of the specific heat in the low temperature region it is natural that the minimum gap should be dominant. On the other hand the value of Δ_0, found from (4.20), which is valid for the isotropic case, gives some average value of the gap. Hence it is clear that the theoretical curve for the isotropic model will give a reduced value of specific heat in the low temperature region, and this is indeed observed (see fig. 3).

4.3. *The Critical Magnetic Field*

The magnitude of the critical field can be found by using the well-known thermodynamic relation

$$H_c^2/8\pi = F_n - F_s, \qquad \text{(4.29)}$$

and we now calculate the free energy F_s in the superconducting state, equal to

$$F_s = E - TS. \qquad \text{(4.30)}$$

The energy E is given by formula (4.6), and the entropy by (4.7), but before substituting the expressions for E and S in (4.30) we change their form slightly. On substitution of the expressions (4.5) for u_k and v_k, and on simplification using (4.3), the expression for the energy becomes

$$\begin{aligned} E = {} & \sum_k \{\xi_k - \sqrt{(\xi_k^2+\Delta^2)} + \tfrac{1}{2}\Delta^2(\xi_k^2+\Delta^2)^{-1/2}\} \\ & + \sum_k \{2n_k\sqrt{(\xi_k^2+\Delta^2)} - \Delta^2 n_k(\xi_k^2+\Delta^2)^{-1/2}\}. \qquad \text{(4.31)} \end{aligned}$$

After a simple integration by parts the entropy (4.7) can be written as[†]

$$S_s = \frac{2}{T}\sum_k [2n_k\sqrt{(\xi_k^2+\Delta^2)} - \Delta^2 n_k/\sqrt{(\Delta^2+\xi_k^2)}]. \qquad \text{(4.32)}$$

Substituting (4.31) and (4.32) in the expression for F_s, we find

$$F_s = \sum_k \{\xi_k - \sqrt{(\xi_k^2+\Delta^2)} + \tfrac{1}{2}\Delta^2/\sqrt{(\xi_k^2+\Delta^2)}\} - \tfrac{1}{2}S_s T. \qquad \text{(4.33)}$$

The summation can be rewritten in the form

$$\sum \to 2\sum_{\xi_k<0}\xi_k + \sum\{|\xi_k| - \sqrt{(\xi_k^2+\Delta^2)} + \tfrac{1}{2}\Delta^2(\Delta^2+\xi_k^2)^{-1/2}\}. \qquad \text{(4.34)}$$

[†] Here we denote the entropy in the superconducting state by the index *s*.

The first sum in (4.34) is independent of the energy gap and since it is a constant common to both the normal and superconducting states, it may be omitted. The second sum may be written in the form of a convergent integral, the magnitude of which is

$$-\tfrac{1}{4}\nu\Delta^2.$$

Thus we finally get

$$F_s = -\tfrac{1}{4}\nu\Delta^2 - \tfrac{1}{2}S_s T, \qquad (4.35)$$

and since the free energy in the normal state is given by

$$F_n = -\tfrac{1}{2}S_n T, \qquad (4.36)$$

we find, using (4.29),

$$H_c^2/8\pi = \tfrac{1}{4}\nu\Delta^2 + \tfrac{1}{2}(S_s - S_n)T. \qquad (4.37)$$

This formula relates the critical magnetic field to the energy gap and the entropy difference between the superconducting and the normal states. Hence at $T=0$ we obtain a relation between the energy level separation Δ_0 and the critical field H_{c0}:

$$H_{c0} = \Delta_0\sqrt{(2\pi\nu)}. \qquad (4.38)$$

For T near to zero S_s is exponentially small, while S_n is given by

$$S_n = \tfrac{1}{3}\pi^2\nu T$$

So for the temperature variation of H_c in the neighbourhood of $T=0$ we find

$$H_c = H_{c0}(1 - \tfrac{1}{3}\gamma^2 T^2/T_c^2). \qquad (4.39)$$

The temperature variation of H_c near T_c is found by substituting (4.26) in (4.37). The quadratic terms in Δ cancel and taking the first non-vanishing term we get

$$H_c^2/8\pi = q\nu\Delta^4/16\,T_c^2, \qquad (4.40)$$

and using (4.22) and (4.38) this gives

$$H_c = H_{c0} \times 2{\cdot}35\,(1 - T/T_c) \qquad (4.41)$$

as the temperature variation of H_c near T_c.

This temperature dependence of H_c near T_c is in agreement with the experimental data (Shoenberg 1955) which are usually described over the whole temperature region by the formula

$$H_c = H_{c0}(1 - T^2/T_c^2). \qquad (4.42)$$

It is evident that these two formulae do not give widely different values for H_c when T is near T_c, and for temperatures close to $T=0$ there is also good agreement between theory and experiment, as can be seen by comparing formulae (4.41) and (4.42).

To conclude this section we give some relations which are obtained by differentiation of (4.37):

$$S_c - S_n - (C_s - C_n) = \tfrac{1}{2}\partial\Delta^2/\partial T, \qquad (4.43)$$

$$H_c^2/8\pi = (\nu/4T)\,\partial(T\Delta^2)/\partial T + \tfrac{1}{2}T(C_s - C_n). \qquad (4.44)$$

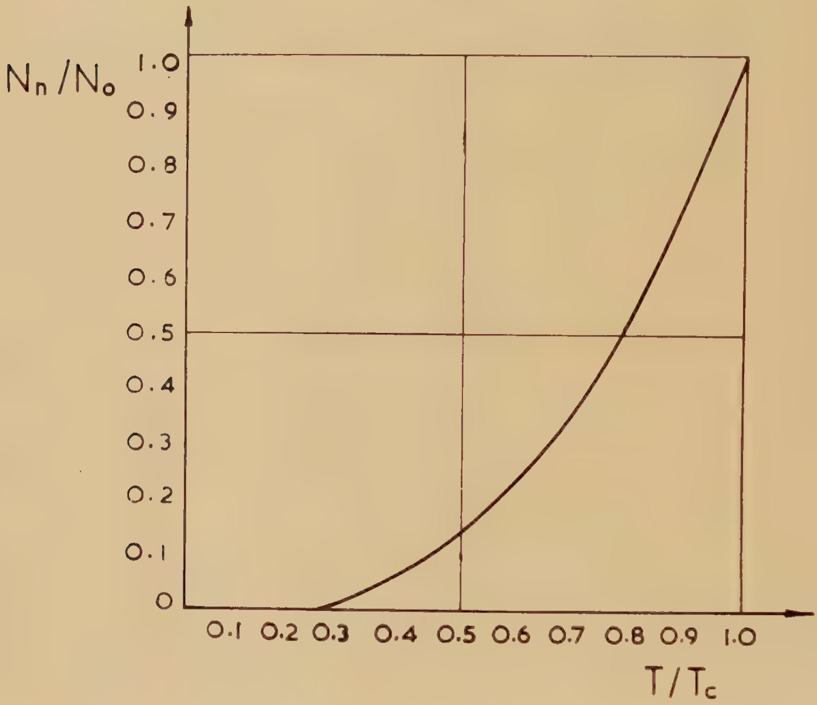
The relation (4.43) is noteworthy in that it enables us to express the entropy in the superconducting state as a certain integral of the derivative $\partial\Delta/\partial T$; thus writing C_s in (4.43) as $T\,\partial S_s/\partial T$ and integrating we find

$$S_s = T\int_0^T \frac{1}{T^2}\frac{d\Delta^2}{dT}\,dT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.43')$$

4.4. *The Number of 'Normal' Electrons*

The so-called 'number of normal electrons' is important in the description of the behaviour of superconductors in magnetic fields in certain cases (in the so-called London region). This quantity may be defined as a coefficient of proportionality between the total momentum of the excitations and their macroscopic velocity. The total excitation momentum is equal to

Fig. 4



$$\mathbf{P} = \sum_k \mathbf{k}\,(n_{k0} + n_{k1}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.45)$$

In the presence of macroscopic motion the argument of the function n_k will not be $\epsilon(k)$, but $\epsilon(k) - \mathbf{ku}$. Treating $\mathbf{u}$ as small, and expanding $n(\epsilon - \mathbf{ku})$ in a series in $\mathbf{ku}$, we find

$$P = -\frac{2}{T}\sum \mathbf{k}(\mathbf{ku})\frac{\partial n_k}{\partial \epsilon(k)} = -\frac{k_0{}^2\nu}{3T}\mathbf{u}\int_{-\infty}^{\infty}\frac{\partial n}{\partial \epsilon}\,d\zeta. \quad . \quad . \quad (4.46)$$

It is now simple to find the ratio of the number of normal electrons in the superconducting state of the total number of 'free' electrons

$$\frac{N_n}{N_0} = -\int_{-\infty}^{\infty} \frac{\partial n}{\partial \epsilon} d\xi. \qquad (4.47)$$

Introducing the new variable $\xi = \Delta \cosh \phi$, this formula can be rewritten as

$$\frac{N_n}{N_0} = 2\frac{\Delta}{T}\int_0^{\infty} \frac{\cosh \phi \, d\phi}{(\exp[\Delta \cosh \phi/T]+1)(\exp[-\Delta \cosh \phi/T]+1)}. \qquad (4.48)$$

Differentiating (3.16) with respect to the temperature, we note that N_n/N_0 may be expressed in terms of $\partial\Delta/\partial T$ as

$$\frac{N_n}{N_0} = -\frac{1}{T}\frac{\partial \Delta}{\partial T}\bigg/\frac{\partial}{\partial T}\left(\frac{\Delta}{T}\right). \qquad (4.49)$$

Hence we find the following simple relation for the number of 'superconducting' electrons, $N_s = N_0 - N_n$ where

$$\frac{N_s}{N_0} = -1\bigg/\frac{\partial \ln(\Delta/T)}{\partial \ln T}. \qquad (4.50)$$

For $T \rightarrow 0$ the limiting form for N_n/N_0 is

$$N_n/N_0 = (2\pi\Delta_0/T)^{1/2}\exp(-\Delta_0/T), \qquad (4.51)$$

while for $T \rightarrow T_c$ we have

$$1 - N_n/N_0 = 2(T_c - T)/T_c. \qquad (4.52)$$

As for the specific heat the next term in the expansion in powers of $T_c - T$ will be proportional to $(T_c - T)^{3/2}$. The full curve of the temperature variation of $N_n(T)/N_0$ is shown in fig. 4.

§ 5. The Electrodynamic Equations of Superconductors

5.1. *The Absolute Zero* ($T = 0$)

We consider a superconductor in a constant (time-independent) magnetic field, the vector potential of which is

$$\mathbf{A}(\mathbf{r}) = \sum_q \mathbf{A}_\mathbf{q} \exp(i\mathbf{q}\mathbf{r}) \qquad (5.1)$$

and calculate the current caused by this field. To do this we find the change δE in the energy of the system due to the presence of the field, and then use the relation

$$\delta E = -\mathbf{j}\delta\mathbf{A}/c \qquad (5.2)$$

to find the current.

The Hamiltonian for the system in the presence of the field is

$$H_f = H + \frac{1}{2m}\sum a^+(k,\sigma)a(k',\sigma)\left\{-\frac{e}{c}(\mathbf{k}+\mathbf{k}')\,\mathbf{A} + \frac{e^2}{c^2}A^2\right\}. \qquad (5.3)$$

where H is the unperturbed Hamiltonian of the problem (3.1). Next we transform from the particle operators $a(k,\sigma)$ and $a(k,\sigma)$ to the excitation operators $\alpha(k,1)$ and $\alpha(k,0)$ using (3.3), and we find the transformed Hamiltonian $H_f = H + H'$, with

$$H' = \frac{1}{2m}\sum\left[-\frac{e}{c}(\mathbf{k}+\mathbf{k}')\mathbf{A}+\frac{e^2}{c^2}A^2\right][u_k u_{k'}\{\alpha^+(k,1)(k',2)+\alpha^+(k,0)\,\alpha(k,0)\}$$
$$+v_k v_{k'}\{\alpha(-k,0)\,\alpha^+(-k',0)+\alpha(-k,1)\,\alpha^+(-k',1)\}$$
$$+u_k v_{k'}\{\alpha^+(k,1)\,\alpha^+(-k',0)-\alpha^+(k,0)\,\alpha^+(-k',1)\}$$
$$+v_k u_{k'}\{\alpha(-k,0)\,\alpha(k',1)-\alpha(-k,1)\,\alpha(k',0)\}]. \qquad (5.4)$$

It is evident that the change in energy of the system will be only second order in **A** since **A** has no diagonal matrix elements. To find the change in energy it is necessary to take the first approximation of perturbation theory for the quadratic terms in **A**, and the second approximation for the linear terms in **A** which appear in H'. At $T=0$ the non-vanishing diagonal matrix elements contain only terms with the operator product $\alpha\alpha^+$. Thus, taking the diagonal matrix elements of H', we find the energy change in first-order perturbation theory

$$\delta E_{\mathrm{I}} = \sum H'_{kk} = \frac{e^2}{mc^2}\sum_{k,q}\mathbf{A}_{-q}\mathbf{A}_q v_k^2. \qquad (5.5)$$

In the calculation of the second approximation of perturbation theory there are possible transitions in which two excitations with opposite spins are first created, and then annihilated. The matrix element of H' corresponding to the creation of a pair of excitations in accordance with (5.4) is

$$(u_k v_{k-q} - v_k v_{k-q})(2\mathbf{k}-\mathbf{q}, \mathbf{A}\mathbf{q}),$$

and the energy difference between the ground state and the state with two excitations is equal to

$$-(\epsilon_k + \epsilon_{k-q}).$$

Using this, we find for the second approximation of perturbation theory

$$\delta E_{\mathrm{II}} = -\frac{e^2}{4m^2c^2}\sum\frac{(u_k v_{k-q} - v_k u_{k-q})^2(2\mathbf{k}-\mathbf{q}, \mathbf{A}_q)(2\mathbf{k}-\mathbf{q}, \mathbf{A}_{-q})}{\epsilon_k + \epsilon_{k-q}} \quad . \qquad (5.6)$$

and using (5.2), and varying the sum $\delta E_{\mathrm{I}} + \delta E_{\mathrm{II}}$, we find the Fourier component of the current

$$\mathbf{j}_q = \frac{e^2}{mc}\left\{-\sum 2v_k^2\mathbf{A}_q + \frac{1}{2m}\sum_k\frac{(2\mathbf{k}-\mathbf{q})(2\mathbf{k}-\mathbf{q}, \mathbf{A}_q)(v_k u_{k-q}) - v_{k-q}u_k)^2}{\epsilon_k + \epsilon_{k-q}}\right\}. \qquad (5.7)$$

Thus we have a relation between the current **j** and the vector potential **A** which shows clearly that there is in general no local relation of the type of the London equations between the current **j** and the potential **A**. The expression derived for $\mathbf{j}_q$ has one main shortcoming, namely that it is not gauge-invariant, as can be seen if we calculate div **j**, which according to the continuity condition should be zero. In terms of the Fourier components this condition becomes $\mathbf{q}\mathbf{j}_q = 0$, and it is easy to see that in the general case (4.7) does not satisfy this condition. This point, which was not noticed by BCS (1957), is not surprising, since the technique of perturbation theory which was applied is itself not gauge-invariant. Thus, in (5.7) we must understand by $\mathbf{A}_q$ only the transverse part of the potential. In fact the transformation of (3.3) from the operators $\alpha(k, \sigma)$ to the pair of operators $\alpha(k, 1)$ and $\alpha(-k, 1)$ is carried out in such a way that the pair of bound electrons created always has zero momentum, and this last property of the theory is evidently not invariant since the pairs may move in the field. However, a more detailed analysis of this question shows that only the transverse component of the vector potential, which satisfies the condition div $\mathbf{A}=0$, makes a contribution to the current. The transverse nature of the first term in $\mathbf{j}_q$, which arises from δE_{I}, is evident, and as regards the second term, after multiplication by $\mathbf{q}$ and transformation from the variable $\mathbf{k}$ to the variable $\mathbf{k}-\frac{1}{2}\mathbf{q}$ this becomes

$$\frac{2e^2}{m^2c^2}\sum_k \frac{(\mathbf{kq})(\mathbf{kA}_q)(v_{k-\frac{1}{2}q}u_{k+\frac{1}{2}q}-u_{k-\frac{1}{2}q}v_{k+\frac{1}{2}q})}{\epsilon_{k+\frac{1}{2}q}+\epsilon_{k-\frac{1}{2}q}}. \quad . \quad . \quad . \ (5.8)$$

It is easy to see that as a result of integration over the angles of the vector $\mathbf{k}$ this expression will contain the vector potential only in the product $\mathbf{qA}_q$ and consequently, if $(\mathbf{qA}_q)=0$, then $\mathbf{j}_q . \mathbf{q}=0$ also.

The expression (5.7) for the current has a property which is important in the further discussion. This is that for large values of the wave vector $\mathbf{q}$ the energy gap is not of importance so that in this energy region the electrons must behave like free electrons. Thus, since free electrons are not superconducting, the current $\mathbf{j}_q$ must tend to zero as the wave vector $\mathbf{q}$ tends to infinity. We will show in fact that for large values of $\mathbf{q}$ the first and second terms in (5.7) cancel out. To do this we use the symmetrical form for the second term in the curly brackets in (5.7):

$$\sum \rightarrow \frac{2}{m}\sum \frac{k(\mathbf{kA}\ )(v_{k-\frac{1}{2}q}u_{k+\frac{1}{2}q}-v_{k+\frac{1}{2}q}u_{k-\frac{1}{2}q})^2}{\epsilon_{k-\frac{1}{2}q}+\epsilon_{k+\frac{1}{2}q}}.$$

We now express v and u in terms of the quantities

$$\xi_+,\ \ \xi_- \doteq v(|\mathbf{k}\pm\tfrac{1}{2}\mathbf{q}|-k_0),$$

making use of (4.5). For large values of $\mathbf{q}$,

$$\xi_+, \xi_- = \xi \pm \tfrac{1}{2}v_q \cos\theta.$$

θ is here the angle between the vectors $\mathbf{k}$ and $\mathbf{q}$; $\mathbf{q}$ is large but $|\mathbf{q}| \ll k_0$. We find for these large values

$$\sum \rightarrow \frac{2}{m}\sum \mathbf{k}(\mathbf{kA}_q)\frac{1}{|\xi_+|+|\xi_-|}\frac{1}{2}\left\{1-\frac{\xi_+\xi_-}{|\xi_+||\xi_-|}\right\}. \quad . \quad . \quad (5.9)$$

In this sum the only non-zero terms are those in which ξ_+ and ξ_- have opposite signs. Transforming the sum to an integral, we have

$$\sum \rightarrow \frac{2}{m}\int_{-1}^{1} d(\cos\theta)\int \frac{1}{q\cos\theta}\frac{2\pi k^2\,dk}{(2\pi)^3 v}\mathbf{k}(\mathbf{kA}_q)=N\mathbf{A}_q, \quad . \quad (5.10)$$

the limits of the second integral being $k_0 \pm \frac{1}{2}q\cos\theta$. Here N is the total number of electrons (per cm^3), given by

$$N=8\pi k_0{}^3/3(2\pi)^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.11)$$

The first term in the curly brackets in the expression (5.7) for $\mathbf{j}_q$ is evidently equal to $-N\mathbf{A}_q$ and therefore for large $\mathbf{q}$ both terms in $\mathbf{j}_q$ cancel out as stated above.

In future the relation between the current and the transverse component of the potential $\mathbf{A}_q$ will be written in the form

$$\mathbf{d}q = cK(q)\,\mathbf{A}_q/4\pi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.12)$$

with a kernel $K(q)$ which by (5.7) and (5.8) is equal to

$$K(q) = \frac{Ne^2}{mc^2}\left\{1 - \frac{k_0^4}{(2\pi)^3 Nmv}\int \frac{\sin^2\theta\cos^2\theta\, d(\cos\theta)\, d\phi\, d\xi}{\epsilon_+ + \epsilon_-}\left(1 - \frac{\xi_+\xi_- + \Delta_0^2}{\epsilon_+\epsilon_-}\right)\right\}.$$

$$. \quad . \quad . \quad . \quad . \quad . \quad (5.13)$$

In this expression we may integrate with respect to $d\xi$ from $-\infty$ to $+\infty$ and over the angle ϕ, and we get, setting $\mu = \cos\theta$, an expression for the kernel $K(q)$ at $T = 0$,

$$K(q) = \frac{4\pi Ne^2}{mc^2}\,\frac{3\Delta_0}{2|q|v}\int_{-1}^{+1} \frac{\sinh^{-1}(q\mu v/2\Delta_0)(1-\mu^2)\,d\mu}{\sqrt{\{1 + q^2\mu^2v^2/4\Delta_0^2\}}} \quad . \quad (5.14)$$

which as stated above tends to zero for sufficiently large values of q. The field distribution in the superconductor (Meissner effect) may be found if we apply to equation (5.14) the Maxwell equation (div $\mathbf{A} = 0$)

$$\Delta\mathbf{A} = -4\pi\mathbf{j}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.15)$$

Equation (5.12) gives a relation between the Fourier components of the current $\mathbf{j}_q$ and the field potential $\mathbf{A}_q$ for arbitrary values of the wave vector $\mathbf{q}$. In the general case the relation derived is non-local, i.e. the coefficient $K(q)$ for $\mathbf{A}_q$ depends on the magnitude of the vector $\mathbf{q}$, and in coordinate space this corresponds to some integral relation between $\mathbf{j}(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ of the form

$$\mathbf{j}(\mathbf{r}) = \int K(\mathbf{r}-\mathbf{r}')\,\mathbf{A}(\mathbf{r}')\,\mathbf{d}\mathbf{r}'.$$

Thus the value of the current at any point is determined by an integral of the values of the field potential in the neighbourhood of the point. We call such a relation non-local. In the old London theory the function $K(\mathbf{r}-\mathbf{r}')$ had the character of a δ-function ($K(q) = \text{const}$), so that $\mathbf{j}(\mathbf{r})$ was proportional to $\mathbf{A}(\mathbf{r})$, we shall but see that this proportionality holds only for small values of the wave vector. The non-local character of the relation between $\mathbf{j}$ and $\mathbf{A}$ was predicted by Pippard (1953).

5.1. *The Penetration Depth*

We shall now apply eqns. (5.14) and (5.15) to a semi-infinite region, i.e. we shall consider a semi-infinite metal. It is natural to question the validity of (5.14) in this case, since the equation was derived for an infinite medium. Fortunately, however, the situation is favourable as regards this question and the presence of the boundary turns out not to affect the kernel $K(q)$. The fact is that the wavelength of the excitations is small and is of order of magnitude

$$\lambda = 1/K_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.16)$$

i.e. of the interatomic distances. Thus the presence of the boundary will affect only those excitations within a narrow layer at the boundary, of depth of the order of the interatomic distances. Since, the penetration depth is much greater than this, it is natural that the expression (5.12) with $K(q)$ defined by the relation (5.14) should be valid in all cases, i.e. for any spatial configuration.

The second question which arises in the presence of a boundary is connected with the character of the reflection of the excitations at the boundary. It is known that in some problems, for example, in the anomalous skin effect (Reuter and Sondheimer 1948), practically the same results are obtained in the two limiting cases of specular and diffuse reflection. We may hope that in the present case too the character of the reflection of the excitations at the boundary does not materially affect the penetration depth. We shall therefore first discuss the case of specular reflection since it is the more convenient in connection with this problem. The presence of a specularly reflecting boundary enables us to reflect the potential at the boundary, i.e. $A(z)=A(-z)$ (z is in the direction of the normal to the boundary), and in terms of the Fourier components of the potential this condition becomes:

$$A_q=A_{-q}. \tag{5.17}$$

If there is a magnetic field at the boundary of the metal it follows that the derivative $\partial A/\partial z$ will not be continuous across the boundary $z=0$. Thus if $\partial A/\partial z$ were continuous, then for an even function at the boundary ($z=0$) the derivative and consequently the field also would be zero. Since the derivatives $\partial A/\partial z$ at $z=+0$ and $z=-0$ are not equal, the second derivative $\partial^2 A/\partial z^2$ at $z=0$ contains a δ-function of the coordinate z. Therefore for a half-space we must add on the right-hand side of eqn. (5.15) a term $c\delta(z)$ with a coefficient c, the magnitude of which can be easily determined from the boundary conditions. In fact the derivative $\partial A/\partial z$ at $z=0$ is equal to the value of the magnetic field at the boundary, so that the second derivative, must be $2M_0\delta(z)$, and it follows that $c=2M_1$. In the case of a half-space all the quantities depend only on the z coordinate, so rewriting (5.15) in Fourier components and taking into account the presence of the δ-function on the right-hand side, we get

$$q^2A_q=4\pi j_q/c+H_0/\pi. \tag{5.18}$$

Substituting into this the expression (5.12) for j_q and solving the resultant equation for A_q, we find

$$A_q=H_0/\pi\{q^2+K(q)\} \tag{5.19}$$

or, in the coordinate representation

$$A(z)=\frac{2H_0}{\pi}\int_0^\infty\frac{\cos qz\,dq}{q^2+K(q)}. \tag{5.20}$$

Differentiating this with respect to z and taking into account the boundary condition $H=H_0$, for $z=0$, we find an expression for the magnetic field in the semi-infinite metal

$$H(z)=H_0-\frac{2H_0}{\pi}\int_0^\infty\frac{\sin qz\,q\,dq}{q^2+K(q)}. \tag{5.21}$$

Finally we calculate penetration depth δ, which is defined by the relation

$$\delta = \int_0^\infty H\,dz/H_0 = \frac{A(0)}{H_0} = \frac{2}{\pi}\int_0^\infty \frac{dq}{q^2+K(q)} \quad . \quad . \quad . \quad (5.22)$$

and we shall now analyse this expression for the penetration depth in more detail. First we examine the form of the function $K(q)$ for the limits of small and large values of q, and find from (5.14) after some fairly simple calculations, for the two cases

$$K(q) = \frac{4\pi Ne^2}{mc^2}\left(1 - \frac{1}{30}\frac{q^2v^2}{\Delta_0{}^2}\right) \quad . \quad . \quad . \quad . \quad (5.23\,a)$$

$$= \frac{4\pi Ne^2}{mc^2}\frac{3\pi^2}{4qv}\Delta_0\left(1 - \frac{8}{\pi^2}\frac{\ln(qv/\Delta_0)}{qv/\Delta_0}\right). \quad . \quad . \quad . \quad (5.23\,b)$$

The two expressions for $K(q)$ are approximately equal for

$$q_0 \approx 3\pi^2\Delta_0/4v.$$

When the penetration depth δ is small compared to $1/q_0$ (Pippard case), large values of q are important in the integral (5.22), and using (5.23 *b*) we get

$$\delta = \frac{2}{\pi}\left(\frac{4\pi Ne^2}{mc^2}\frac{3\pi^2}{4}\frac{\Delta_0}{v}\right)^{-1/3}\int_0^\infty \frac{dq}{q^3+1} = \frac{4}{3\sqrt{3}}\left(\frac{3\pi^3Ne^2}{mc^2}\frac{\Delta_0}{v}\right)^{-1/3}. \quad (5.24)$$

In the other limiting case (London case), when $\delta \ll 1/q_0$ we use (5.23 *a*) and obtain

$$\delta = (4\pi Ne^2/mc^2)^{-1/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.25)$$

which is the well-known formula of the London theory. It should be noted that for $N \sim 10^{22}$ and $\Delta_0 \sim 5$°K both formulae give approximately the same numerical results for the penetration depth. It turns out that superconductors of both the Pippard and London types occur in practice; thus aluminium and mercury are Pippard metals, while lead and indium are London metals and there are also intermediate cases such as tin.

5.1.1. $T=0$

We now consider a superconductor in a magnetic field at a non-zero temperature. As before the magnetic field is represented by the vector potential **A**, and as for the case when $T=0$ we calculate the change in the energy, using the Hamiltonian (5.4). However, the contribution to the second approximation of perturbation theory will now give not only terms containing the two operators α^+ or α, but also terms containing the product $\alpha^+\alpha$. In the present case the product $\alpha^+(k)\alpha(k')$, which corresponds to the creation of an excitation in the state k and the annihilation of an excitation in the state **k**$'$, can give rise to the necessary matrix elements in the transformation since the system is not in the ground state. Here the action of the operators $\alpha^+(k)$ and $\alpha(k)$ on the ψ-function of the unperturbed state is defined by the following relations

$$\left.\begin{aligned}\alpha^+(k)\psi(\ldots n_k\ldots) &= \sqrt{(1-n_k)}\,\psi(\ldots n_k-1\ldots),\\ \alpha(k)\psi(\ldots n_k\ldots) &= \sqrt{n_k}\,\psi(\ldots n_k+1\ldots).\end{aligned}\right\} \quad (5.26)$$

In the first approximation of perturbation theory the change in energy is

$$\delta E_{\mathrm{I}} = \sum H'_{kk} = \frac{e^2}{mc^2} \sum_{k_2} A_q A_{-q} [v_k{}^2 + (u_k{}^2 - v_k{}^2) n_k]. \quad . \quad (5.27)$$

Since, however, the difference $u_k - v_k$ by (4.5) is an odd function of ξ, the sum $\sum (u_k{}^2 - v_k{}^2) n_k$ is zero. Hence for δE_{I} we get the same formula as before (see (5.5))

$$\delta E_{\mathrm{I}} = (e^2/mc^2) \sum A_q A_{-q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.28)$$

The calculation of the energy change δE_{II} in the second approximation of perturbation theory is also easily carried out. The matrix element of H', corresponding to the creation of pairs of excitations is, by (5.4) and (5.26)

$$(v_k u_{k-q} - u_k v_{k-q})(2k - q, A_q) \sqrt{(1 - n_{k-q})} \sqrt{(1 - n_k)}.$$

The matrix element corresponding to the annihilation of pairs in the unperturbed state is $(u_k v_{k-q} - v_k u_{k-q})(2k - q, A_k) \sqrt{(1 - n_{k-q})} \sqrt{n_k}$, and finally the matrix element corresponding to the simultaneous creation and annihilation of excitations is

$$(u_k u_{k-q} + v_k v_{k-q}) \sqrt{(1 - n_k)} \sqrt{n_{k-q}}.$$

We may now without difficulty write down the second approximation to the energy change as

$$\delta E_{\mathrm{II}} = -\frac{e^2}{4m^2c^2} \sum \frac{(u_k v_{k-q} - v_k u_{k-q})^2 (2\mathbf{k} - \mathbf{q}, \mathbf{A}_q)(2\mathbf{k} - \mathbf{q}, \mathbf{A}_{-q})}{\epsilon_k + \epsilon_{k-q}}$$
$$+ (1 - n_k - n_{k-q}) + \frac{(u_k u_{k-q} + v_k v_{k-q})^2 (2\mathbf{k} - \mathbf{q}, \mathbf{A}_q)(2\mathbf{k} - \mathbf{q}, \mathbf{A}_{-q})(-n_k + n_{k-q})}{\epsilon_k - \epsilon_{k-q}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.29)$$

Transforming from the variable $\mathbf{k}$ to the variable $\mathbf{k} - \frac{1}{2}q$ and taking into account the expression (4.8) for n_k, we get a symmetrical formula for δE:

$$\delta E = \delta E_{\mathrm{I}} + \delta E_{\mathrm{II}} = \frac{e^2}{2mc^2} \Bigg[\sum 2 v_k{}^2 A_q A_{-q}$$
$$- \frac{1}{m} \sum \frac{(u_{k-\frac{1}{2}q} v_{k+\frac{1}{2}q} - v_{k-\frac{1}{2}q} u_{k+\frac{1}{2}q})^2}{\epsilon_{k-\frac{1}{2}q} + \epsilon_{k+\frac{1}{2}q}}$$
$$\times (\mathbf{kA}_q)(\mathbf{kA}_{-q}) \left\{ \tanh \frac{\epsilon_{k-\frac{1}{2}q}}{2T} + \tanh \frac{\epsilon_{k+\frac{1}{2}q}}{2T} \right\}$$
$$- \frac{(u_{k-\frac{1}{2}q} u_{k+\frac{1}{2}q} + v_{k-\frac{1}{2}q} v_{k+\frac{1}{2}q})^3}{\epsilon_{k+\frac{1}{2}q} - \epsilon_{k-\frac{1}{2}q}} (\mathbf{kA}_q)(\mathbf{kA}_q)$$
$$\times \left\{ \tanh \frac{\epsilon_{k+\frac{1}{2}q}}{2T} - \tanh \frac{\epsilon_{k-\frac{1}{2}q}}{2T} \right\} \Bigg]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.30)$$

Varying this with respect to A_{-q}, we find an expression for the Fourier component of the current

$$j_q = -c \delta E / \delta A_{-q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.31)$$

Next we use the expressions (4.5) for u_k and v_k and take into account the fact that $\xi_{k+\frac{1}{2}q}=\xi+qv\cos\theta$ and after some fairly simple transformations we find, where A_q is the transverse component of the potential

$$K(q)=\frac{4\pi Ne^2}{mc^2}A_q\left\{-1+\frac{3}{16\pi}\int\sin^2\theta\,d\cos\theta\int d\phi\int d\xi\right\}$$
$$\times\left\{\frac{1}{\epsilon_++\epsilon_-}\left(1-\frac{\xi_+\xi_-+\Delta^2}{\epsilon_+\epsilon_-}\right)\left(\tanh\frac{\epsilon_+}{2T}+\tanh\frac{\epsilon_-}{2T}\right)\right.$$
$$\left.+\frac{1}{\epsilon_+-\epsilon_-}\left(1+\frac{\xi_+\xi_-+\Delta^2}{\epsilon_+\epsilon_1}\right)\left(\tanh\frac{\epsilon_+}{2T}-\tanh\frac{\epsilon_-}{2T}\right)\right\}. \quad (5.32)$$

in which the argument $\mathbf{k}+\frac{1}{2}\mathbf{q}$ is denoted by the index $+$, and the argument $\mathbf{k}-\frac{1}{2}\mathbf{q}$ by the index $-$.

As for $T=0$ the relation (5.32) obtained between the vector potential and the Fourier component of the current is of non-local character, the value of $\mathbf{j}(\mathbf{r})$ at any point being determined by the values of the field potential $\mathbf{A}(\mathbf{r})$ over a certain region around this point. We now transform the expression obtained for $K(q)$; first we collect the terms with $\tanh\epsilon_+$ and $\tanh\epsilon_-$ in (5.32), and then integrate with respect to $d\phi$ and then integrate a part of the terms with respect to $d\xi$. As a result some of the terms cancel and we find

$$K(q)=\frac{4\pi Ne^2}{mc^2}\left(\frac{3\Delta^2}{8qv}\right)\int_{-1}^{1}\int_{-\infty}^{\infty}\frac{\sin^2\theta\,d\cos\theta}{\xi\cos\theta}$$
$$+\left[\frac{\tanh(\epsilon_+/2T)}{\epsilon_+}-\frac{\tanh(\epsilon_-/2T)}{\epsilon_-}\right]d\xi. \quad . \quad . \quad (5.33)$$

The integration of (5.33) cannot be carried further in the general case, so we now consider only the limiting cases of large and small values of q. For large values of q the region of small values (near to zero) of ξ and $\mu=\cos\theta$ are important, and we may therefore put ξ and μ equal to zero in the slowly varying function $\tanh(\epsilon/2T)$ in the integral (5.33). We then get

$$K(q)=\frac{4\pi Ne^2}{mc^2}\left(\frac{3\Delta}{2qv}\right)\int_0^1\frac{d\mu}{\mu}\int_0^\infty\frac{d\xi}{\xi}\left(\frac{1}{\epsilon_1}-\frac{1}{\epsilon_1}\right)\tanh\left(\frac{\Delta}{2T}\right), \quad . \quad (5.34)$$

and further integration may be carried out in terms of elementary functions. After a change of variable from ξ to $1/\eta$, the integration with respect to $d\eta$ is elementary. In the resulting integral with respect to $d\eta$ we make the substitution $qv\mu/2\Delta=\sinh\chi$, and find

$$K(q)=\frac{12\pi}{mc^2}\frac{\Delta}{qv}\int_0^\infty\frac{\chi\,d\chi}{\sinh\chi}\tanh\frac{\Delta}{2T}. \quad . \quad . \quad . \quad (5.35)$$

Finally, carrying out this simple integration, we get

$$K(q)=\frac{3\pi^3Ne^2}{mc^2}\frac{\Delta}{qv}\tanh\frac{\Delta}{2T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.36)$$

This formula differs from (5.23) only in the replacement of Δ_0 by

$$\Delta\tanh(\Delta/2T).$$

We now obtain a formula for the limiting case of small q; this can be obtained most easily from the initial eqn. (5.32), which gives

$$K(q)=\frac{4\pi Ne^2}{mc^2}\left\{1-\frac{1}{2}\int\frac{\partial}{\partial\epsilon}\left(\tanh\frac{\epsilon}{2T}\right)d\xi\right\}. \quad . \quad . \quad (5.37)$$

But $\frac{1}{2}(\partial/\partial\epsilon)\tanh(\epsilon/2T)$ is simply $-\partial n/\partial\epsilon$ and by (4.47) $-\int(\partial n/\partial\epsilon)\,d\xi$ is equal to the ratio of the number of normal electrons to the total number of electrons. Thus for $q\rightarrow 0$ we have

$$K(q)=4\pi N_s e^2/mc^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.38)$$

where the number of superconducting electrons N_s is given by

$$N_s=N(1+\int(\partial n/\partial\epsilon)\,d\xi). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.39)$$

Near $T=T_c$, N_s changes linearly with temperature, and by (4.52) and (5.38) $K(q)$ is in this region given by

$$K(q)=\frac{4\pi Ne^2}{mc^2}\left(2\frac{T_c-T}{T_c}\right) \quad . \quad . \quad . \quad . \quad . \quad (5.40)$$

while, for large values of q, $K(q)$ by (4.22) and (5.36) is

$$K(q)=\frac{3\pi^3 Ne^2}{mc^2}\frac{\Delta_0}{qv}\left\{2{\cdot}65\frac{T_c-T}{T_c}\right\}. \quad . \quad . \quad . \quad . \quad (5.41)$$

The value q_0, for which the two formulae coincide is

$$q_0\simeq 10\Delta_0/v, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.42)$$

while for q_0 at $T=0$ the corresponding value of q is from (5.23) approximately $7{\cdot}5\Delta_0/v$. Thus we arrive at the conclusion, which as we shall see later is of fundamental importance, that the magnitude of the limiting wave vector q_0, separating the regions of large and small values of q, approximately is independent of temperature.

The magnitude of the penetration depth at $T=0$ is as at $T=0$ determined by (5.22).

When the penetration depth is small in the sense $\delta\ll 1/q_0$, we get from (5.36)

$$\delta=\frac{4}{3\sqrt{3}}\left\{\frac{3\pi^3 Ne^2}{mc^2}\frac{\Delta}{v}\tanh\frac{\Delta}{2T}\right\}^{-1/3}=\delta_{T=0}\left\{\frac{\Delta}{\Delta_0}\tanh\frac{\Delta}{2T}\right\}^{-1/3}. \quad (5.43)$$

In the opposite limiting case $\delta\gg 1/q_0$, using (5.38), we get the well-known formulae of the London theory

$$\delta=\left\{\frac{4\pi N_s e^2}{mc^2}\right\}^{-1/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.44)$$

Evidently for T near to T_c this last limiting case will always apply, i.e. the London formulae for δ will be valid. The observed temperature dependence of the penetration depth is often described by the empirical formula

$$\delta=\delta_{\mathrm{OL}}\left\{1-\frac{T^4}{T_c{}^4}\right\}^{-1/2}, \quad \delta_{\mathrm{OL}}=\left\{\frac{4\pi Ne^2}{mc^2}\right\}^{-1/2}, \quad . \quad . \quad (5.45)$$

while near T_c the theoretical formula is of the form

$$\delta=\delta_{\mathrm{OL}}/\sqrt{\{2(1-T/T_c)\}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.46)$$

which is $2^{-1/2}$ times as large as the limiting form of (5.45).

Since the binding energy of an electron pair is approximately Δ_0, the width of the region in momentum space which characterizes a pair is Δ_0/v and consequently the linear dimensions of a pair must be of order of magnitude v/Δ_0. In fact the limiting wave vector can be considered as providing a more accurate measure of the dimensions of a pair; thus corresponding to the wave vector q_0 the length

$$\lambda_0 = 1/q_0 \sim v/8\Delta_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.47)$$

is a characteristic parameter of the theory.

The old London theory is valid in the case when the penetration depth is greater than λ_0. In this case only the wave vectors $q < q_0$ are important in the kernel $K(q)$, and the relation between $\mathbf{j}$ and $\mathbf{A}$ becomes local (the coefficient of proportionality between $\mathbf{j}_q$ and $\mathbf{A}_q$ is independent of q). Thus the London theory is valid when the dimensions of a pair are small compared to the penetration depth. On the other hand, when the dimensions of the pair are large compared to the penetration depth (Pippard case), the new theory is valid, in which the relation between $\mathbf{j}$ and $\mathbf{A}$ is non-local. It is interesting that the characteristic length 'the size of a pair' is approximately independent of the temperature.

5.1.2. *Diffuse scattering*

Up to now, in the calculations of the penetration depth, we have assumed specular reflection in the scattering of electrons from the surface of a metal. We now consider the other limiting case in which the electrons are reflected diffusely; this can be easily calculated if we use the results of the paper by Reuter and Sondheimer (1948) on the anomalous skin effect. If we were to rewrite (5.18), which defines the potential A in the coordinate representation, then, as we have already said, it would become

$$\Delta \mathbf{A}(\mathbf{r}) = -\int K(\mathbf{r}-\mathbf{r}')\mathbf{A}(\mathbf{r}')d\mathbf{r}' \quad . \quad . \quad . \quad . \quad . \quad (5.48)$$

with a kernel $K(\mathbf{r}-\mathbf{r}')$, the Fourier component of which is $K(q)$. For specular reflection the region of integration is from $-\infty$ to ∞ (A in this case is reflected in the second half of space). For diffuse scattering, however, the region of integration evidently extends from 0 to ∞; and the Fourier method is no longer applicable in the solution of the equation, and it is necessary to use the Wiener–Hopf method. We use the results of Reuter and Sondheimer (1948) directly and write the formula for the penetration depth in the diffuse case

$$\delta = \pi \Big/ \int_0^\infty dq \ln\left\{1 + \frac{1}{q^2}K(q)\right\}. \quad . \quad . \quad . \quad . \quad . \quad (5.49)$$

In the London region $K(q)$ is given by formula (5.38) and on integration by parts we get

$$\delta = \{4\pi N_s e^2/mc^2\}^{-1/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.50)$$

In the other limiting case (Pippard region) $K(q)$ is given by (5.36). Substituting for $K(q)$ in (5.51) and integrating by parts, we get

$$\delta=\frac{\sqrt{3}}{2}\bigg/\left\{\frac{3\pi^3 Ne^2}{mc^2}\frac{\Delta}{v}\tanh\frac{\Delta}{2T}\right\}^{1/3} \quad . \quad . \quad . \quad . \quad . \quad (5.51)$$

As was expected the penetration depth in the London region does not depend on the type of reflection. In the Pippard region (small penetration depths) we get, by comparing (5.43) and (5.51), the relation

$$\delta_{\mathrm{diff}}/\delta=9/8 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.52)$$

so that even in this case the dependence on the type of reflection is small.

5.1.3. *Remarks on the properties of superconductors of finite size*

In the case just considered, of a superconductor filling half of space, the vector potential $\mathbf{A}$ automatically satisfies the condition $\operatorname{div}\mathbf{A}=0$, and, as followed from (5.7), the condition $\operatorname{div}\mathbf{j}=0$, necessary for solutions in stationary conditions is satisfied. This point needs some discussion for finite conductors of arbitrary form, where the condition $\operatorname{div}\mathbf{A}=0$ is indeed sufficient, but not necessary for the fulfilment of the conservation condition $\operatorname{div}\mathbf{j}=0$. This in the general case of superconductors of arbitrary shape it is necessary to solve the complete system of equations, consisting of the Maxwell equation and eqn. (5.32) for the superconducting current

$$\left.\begin{aligned}\operatorname{curl}\operatorname{curl}\mathbf{A}&=-4\pi\mathbf{j}/c\\ \mathbf{d}q&=cK(q)\mathbf{A}_q/4\pi.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5.53)$$

In agreement with (5.53) we have at the conservation equation for the current

$$\operatorname{div}\mathbf{j}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.54)$$

In the general case the vector potential for this will no longer satisfy the condition $\operatorname{div}\mathbf{A}=0$.

As an example of the problem of a superconductor of finite size we will calculate the magnetic moment in a constant magnetic field H_0, of a superconducting sphere of radius compared to the penetration depth. For the London region the solution, as is well known, is

$$M=-a^5H_0/30\delta_L^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.55)$$

where a is the radius of the sphere.

We shall now solve this problem for the Pippard region. In the coordinate representation (5.32) may be written as (Bardeen *et al.* 1957)

$$\mathbf{d}(\mathbf{r})=B_p\int\frac{\mathbf{n}(\mathbf{n}\,.\,\mathbf{A}(\mathbf{r}'))}{R^2}d^3\mathbf{r}' \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.56)$$

where $R=|\mathbf{r}-\mathbf{r}'|$, $\mathbf{n}$ is a unit vector in the direction of $\mathbf{R}$, and B_p is a constant given by

$$B_p=\frac{3}{4}\frac{Ne^2}{mc}\frac{\Delta}{v}\tanh\frac{\Delta}{2T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.57)$$

Since the body is small compared to the penetration depth, we may avoid solving of the Maxwell equation since the vector potential $\mathbf{A}(\mathbf{r})$ differs little from its value in the absence of the sphere. In a constant magnetic field H_0 the vector potential is

$$\mathbf{A}(\mathbf{r})=\tfrac{1}{2}[\mathbf{H}_0 . \mathbf{r}]. \qquad (5.58)$$

For this special case $n(\mathbf{A}(\mathbf{r}')-\mathbf{A}(\mathbf{r}))=0$ and therefore $\mathbf{A}(\mathbf{r}')$ in (5.57) may be replaced by $\mathbf{A}(\mathbf{r})$ and

$$\mathbf{j}(r)=B_p\int\frac{\mathbf{n}(\mathbf{n}\mathbf{A}(\mathbf{r}))\,d^3\mathbf{r}'}{R^2}. \qquad (5.59)$$

The conservation law $\operatorname{div}\mathbf{j}=0$ can also be written in the form of a boundary condition for the normal component of the current at the surface of the body,

$$j_n=0, \qquad (5.60)$$

and it is evident by symmetry that this condition will be automatically satisfied for a sphere.

We now use the following simple transformation

$$\frac{\mathbf{n}(\mathbf{n}\mathbf{A})}{R^2}=\tfrac{1}{2}\left\{\mathbf{A}\operatorname{div}\frac{\mathbf{n}}{R}-(\mathbf{A}\nabla)\frac{\mathbf{n}}{R}\right\}, \qquad (5.61)$$

and in (5.59) transform to an integration over the surface. Thus we then find

$$\mathbf{j}(\mathbf{r})=\tfrac{1}{2}B_p\left\{\mathbf{A}(\mathbf{r})\int\frac{\mathbf{n}\,ds}{R}-\int(\mathbf{A}\,d\mathbf{r})\frac{\mathbf{n}}{R}\right\}. \qquad (5.62)$$

The two integrals in (5.62) may be evaluated by introducing the angles χ between $\mathbf{r}$ and $d\mathbf{r}$, θ, the polar angle with respect to $\mathbf{r}$ as polar axis, and ϕ, the azimuthal angle. In the second integral, since it is evident that $\mathbf{j}$ will have the same direction as $\mathbf{A}$, only the component of $\mathbf{n}$ in the $\mathbf{A}$ direction need be taken, i.e. $\sin(\theta+x)\sin\phi$, so that

$$\mathbf{j}=\tfrac{1}{2}B_p\mathbf{A}(\mathbf{r})\left\{\int_0^\pi\int_0^{2\pi}\frac{a^2}{R}\cos\chi\,d(\cos\theta)\,d\phi\right.$$
$$\left.-\int_0^R\int_0^{2\pi}\frac{a^2}{R}\sin(\theta+\chi)\sin^2\theta\sin^2\phi\,d\theta\,d\phi\right\}. \qquad (5.63)$$

Making use of the relations

$$\cos\theta=(r^2+a^2-R^2)/2ar, \quad \cos\chi=(R^2+a^2-r^2)/2aR$$
$$\sin(\theta+\chi)=a\sin\theta/R, \qquad (5.64)$$

the integrals reduce after integration over ϕ to simple integrals over R between the limits $a-r$ and $a+r$. Finally we find, on substituting for $\mathbf{A}$ from (5.58),

$$\mathbf{j}=\frac{\pi}{4}\frac{B_p(1+r)}{r}\left\{\frac{(a^2-r^2)(a^2+3r^2)}{4r^2}\ln\frac{a+r}{a-r}+\frac{3ar}{2}-\frac{a^3}{2r}\right\}. \qquad (5.65)$$

The calculation of the magnetic moment of the sphere

$$M=\tfrac{1}{2}\int[\mathbf{j}\mathbf{r}]\,dV \qquad (5.66)$$

is now elementary. We substitute (5.64) for $\mathbf{j}$ in (5.65) and after a simple integration find

$$M = -H_0\pi^2 a^6 B_p/9. \qquad (5.67)$$

Making use of (5.51) and (5.57), we have that

$$B_p = 3\sqrt{3}/32\pi^3\delta p^3,$$

and so finally, for the Pippard case and for $a \ll \delta_p$ we have†

$$M = -H_0\sqrt{3}a^6/96\pi\delta^3 p. \qquad (5.68)$$

While in the London case the magnetic moment of the sphere is proportional to the square of a/δ_L, in the Pippard case it is proportional to the cube of the ratio a/δ_p.

§ 6. THE BEHAVIOUR OF SUPERCONDUCTORS IN A PERIODIC (HIGH-FREQUENCY) FIELD (Landau 1956)

The behaviour of superconductors in a high-frequency field can be calculated in the same way as for a constant field case. Thus considering a superconductor in a magnetic field which varies with frequency ω, we write the vector potential of the field as

$$\mathbf{A}(\mathbf{r}'t) = \sum \mathbf{A}_q \exp(i\mathbf{qr} - i\omega t). \qquad (6.1)$$

We next find the current operator; from (5.4) we have

$$\begin{aligned}\gamma = (-e/2mc)\sum(k+k'-2eA/c)\{&u_k u_{k'}[\alpha^+(k,1)\alpha(k',1)+\alpha^+(k,0)\alpha(k',0)]\\ &+v_k v_{k'}[\alpha(-k,0)\alpha^+(-k',0)+\alpha(-k,1)\alpha^+(-k',1)]\\ &+u_k v_{k'}[\alpha^+(k,1)\alpha^+(-k',0)-\alpha^+(k,0)\alpha^+(-k',1)]\\ &+v_k u_{k'}[\alpha(-k,0)\alpha(k',1)-\alpha(k,1)\alpha(k',0)]\}. \qquad (6.2)\end{aligned}$$

The matrix element of the current operator may be found according to the standard formulae of perturbation theory for a time dependent perturbation (Landau and Lifshitz 1948). We thus find

$$\begin{aligned}\mathbf{j}_q = -\frac{e^2}{2m^2c^2}\mathbf{k}(\mathbf{kA}_q)\sum\Big\{&(u_{k-\frac{1}{2}q}v_{k+\frac{1}{2}q}-v_{k-\frac{1}{2}q}u_{k+\frac{1}{2}q})^2\\ &\times\left(\frac{1}{\epsilon_{k+\frac{1}{2}q}+\epsilon_{k-\frac{1}{2}q}+\omega}+\frac{1}{\epsilon_{k+\frac{1}{2}q}+\epsilon_{k-\frac{1}{2}}-\omega}\right)\\ &\times\left(\tanh\frac{\epsilon_{k-\frac{1}{2}q}}{2T}+\tanh\frac{\epsilon_{k+\frac{1}{2}q}}{2T}\right)+\text{a similar term}\Big\}. \qquad (6.3)\end{aligned}$$

Using now the expression (4.5) we finally get

$$j_q = cK(q,\omega)A_q/4\pi, \qquad (6.4)$$

$$\begin{aligned}K(q,\omega) = \frac{4\pi Ne^2}{mc^2}\Big\{1-\frac{1}{2mN}\sum k_i k_k\Big[&\left(1-\frac{\xi_-\xi_++\Delta^2}{\epsilon_-\,\epsilon_+}\right)\left(\tanh\frac{\epsilon_+}{2T}+\tanh\frac{\epsilon_-}{2T}\right)\\ &\times\left(\frac{1}{\epsilon_++\epsilon_-+\omega}+\frac{1}{\epsilon_++\epsilon_--\omega}\right)+\left(1+\frac{\xi_-\xi_++\Delta^2}{\epsilon_-\epsilon_+}\right)\\ &\times\left(\tanh\frac{\epsilon_+}{2T}-\tanh\frac{\epsilon_1}{2T}\right)\left(\frac{1}{\epsilon_++\epsilon_-+\omega}+\frac{1}{\epsilon_+-\epsilon_--\omega}\right)\Big]\Big\}. \qquad (6.5)\end{aligned}$$

---

† This result was first obtained by Whitehead (1956); note that δp is the same as Pippard's (and Whitehead's) λd.

Further we take into account the fact that $(\mathbf{qA}_q)=0$ and calculate from $K(q,\omega)$ the value $K(q,0)$ for $q=0$, which is given by formula (5.32). We note also that the function $K(q,\omega)$ is complex, the imaginary part of this function may be found from the damping condition, which is taken into account in (6.5) by a small positive imaginary increment $i\delta$ to ω. We then obtain

$$\begin{aligned}\widetilde{K}(q,\omega) &= K(q,\omega)-K(q,0)\\ &= \frac{3\pi Ne^2}{4mc^2}\int_0^1 \sin^2\theta\, d\cos\theta \int d\xi \Bigg[\left(1-\frac{\xi_+\xi_-+\Delta^2}{\epsilon_+\epsilon_-}\right)\\ &\times\{\tanh(\epsilon_+/2T)+\tanh(\epsilon_-/2T)\}\\ &\times\{(\epsilon_++\epsilon_-+\omega+i\delta)^{-1}+(\epsilon_++\epsilon_--\omega-i\delta)^{-1}-2(\epsilon_+\pm\epsilon_-)^{-1}\}\\ &+\left(1+\frac{\xi_+\xi_-+\Delta^2}{\epsilon_+\epsilon_-}\right)\{\tanh(\epsilon_+/2T)-\tanh(\epsilon_-/2T)\}\\ &\times\{(\epsilon_+-\epsilon_-+\omega+i\delta)^{-1}+(\epsilon_+-\epsilon_--\omega-i\delta)^{-1}-2(\epsilon_+-\epsilon_-)^{-1}\}\Bigg], \qquad (6.6)\end{aligned}$$

and using the relation

$$1/(x\pm i\delta)=1/x\pm i\delta(x), \qquad (6.7)$$

we can find the real and imaginary parts of $K(q,\omega)$. If we introduce the following notation

$$K(q,\omega)=(3e^2N\Delta/4cmvq)Q(q,\omega) \qquad (6.8)$$

and transform from the variables ξ and θ to the variables $\epsilon_1=\epsilon_+/\Delta$, $\epsilon_2=\epsilon_-/\Delta$, we find for large values of q

$$\begin{aligned}Q(\omega)-Q(0) &= \tfrac{1}{2}\int_1^\infty ({\epsilon_1}^2-1)^{-1/2}\,d\epsilon_1 \int_1^\infty ({\epsilon_2}^2-1)^{-1/2}\,d\epsilon_2\\ &\times[(1-\epsilon_1\epsilon_2)\{\tanh(\Delta\epsilon_1/2T)+\tanh(\Delta\epsilon_2/2T)\}\\ &\times\{(\epsilon_1+\epsilon_2+\tilde{\omega}-i\delta)^{-1}+(\epsilon_1+\epsilon_2-\tilde{\omega}-\delta)^{-1}\\ &-2(\epsilon_1+\epsilon_2)\}-(1+\epsilon_1\epsilon_2)\{\tanh(\Delta\epsilon_2/2T)-\tanh(\Delta\epsilon_2/2T)\}\\ &\times\{(\epsilon_1-\epsilon_2+\tilde{\omega}+i\delta)^{-1}+(\epsilon_1-\epsilon_2-\tilde{\omega}-i\delta)^{-1}\\ &-2(\epsilon_1-\epsilon_2)^{-1}\}] \qquad (6.9)\end{aligned}$$

where $\tilde{\omega}=\omega/\Delta$.

6.1. *The Pippard Limiting Case*

It is not possible to carry out further calculations without more concrete assumptions as to the values of the important parameters of the problem. Here the most important circumstance is that apparently for most superconductors the penetration depth is much less[†] than v/Δ, i.e. $vq\gg\Delta$. This inequality becomes invalid only in the neighbourhood of the transition point T_c, where there is a region for which $vq\ll\Delta$. In the main region the electrodynamics are based on the equation suggested by Pippard, while in the second region (near T_c) the London equations are applicable (London region)†.

[†] Strictly speaking, the strong inequality $vq\gg\Delta$ is not valid. The applicability of the formulae which are obtained in this limiting case is however guaranteed by the presence of considerable numerical factors.

For the case of an alternating field the London region becomes narrower. This is clear if only from the fact that the normal metal must always be of the Pippard type, since in it $\Delta = 0$, and so it follows that the London region cannot continue right up to the transition point. Leaving aside for the present a detailed discussion of this question, we shall now consider how (6.6) may be simplified in the Pippard region.

In (5.9) we make the change of variables $\epsilon_1 \rightleftharpoons \epsilon_2$, so that all the terms become proportional to $\tanh(\Delta\epsilon_1/2T)$. Collecting terms, we arrive at the following expression:

$$Q(\omega) - Q(0) = \int_1^\infty \tanh\left(\frac{\Delta\epsilon_1}{2T}\right)\frac{d\epsilon_1}{\sqrt{(\epsilon_1{}^2-1)}}\int_1^\infty \frac{\epsilon_2 d\epsilon_2}{\sqrt{(\epsilon_2{}^2-1)}}$$
$$\times\left\{\frac{\epsilon_1(\epsilon+\tilde{\omega})+1}{(\epsilon_1+\tilde{\omega}+i\delta)^2-\epsilon_2{}^2} + \frac{\epsilon_1(\epsilon_1-\tilde{\omega})+1}{(\epsilon_1-\tilde{\omega}-i\delta)^2-\epsilon_2{}^2} - \frac{2(\epsilon_1{}^2+1)}{\epsilon_1{}^2-\epsilon_2{}^2}\right\}. \quad (6.10)$$

This expression can easily be integrated with respect to ϵ_2. Supposing for definiteness that $\omega > 0$, and separating real and imaginary parts, we have‡

$$Q(\omega) = \pi\int_{\max(1,\tilde{\omega}-1)}^{1+\omega} \tanh\frac{\Delta\epsilon}{2T}\frac{\epsilon(\epsilon-\tilde{\omega})+1}{\sqrt{[(\epsilon^2-1)\{1-\epsilon(\epsilon-\tilde{\omega})^2\}]}}$$
$$-i\pi\theta(\tilde{\omega}-2)\int_1^{\tilde{\omega}-1} \tanh\frac{\Delta\epsilon}{2T}\frac{\epsilon(\tilde{\omega}-\epsilon)-1}{\sqrt{[(\epsilon^2-1)\{(\tilde{\omega}-c)^2-1\}]}}d\epsilon$$
$$-i\pi\int_1^\infty \tanh\left\{\frac{\Delta}{2T}(\epsilon+\tilde{\omega}) - \tanh\frac{\Delta\epsilon}{2T}\right\}\frac{\epsilon(\omega+\epsilon)+1}{\sqrt{[(\epsilon^2-1)\{(\epsilon+\tilde{\omega})^2-1\}]}}d\epsilon \quad . \quad (6.11)$$

where $\theta(x) = 1 (x > 0)$ or $0 (x < 0)$, and $\tilde{\omega} = \omega/\Delta$.

First of all we consider the case $T = 0$. In this case (6.11) simplifies considerably and it is easy to see that it can be expressed in terms of the elliptic integrals:

$$Q(\tilde{\omega}) = \begin{cases} 2\pi E(\tfrac{1}{2}\tilde{\omega}) \quad \tilde{\omega} < 2 \\ \pi[\tilde{\omega}E(2/\tilde{\omega}) - (\tilde{\omega}^2-4)\tilde{\omega}^{-1}K(2/\omega) - i\pi\theta(\tilde{\omega}-2)] \\ \times[\tilde{\omega}E(\sqrt{1-(2/\omega)^2}) - 4\tilde{\omega}^{-1}K(\sqrt{1-2/\tilde{\omega}^2})] \quad \tilde{\omega} > 2. \end{cases} \quad . \quad . \quad . \quad (6.12)$$

For low frequencies the limiting value of this expression is

$$Q(\tilde{\omega}) = \pi^2\{1-(\omega^2/4)^2\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.13)$$

For $\tilde{\omega} \gg 1$ we have

$$Q(\tilde{\omega}) = \pi^2/\tilde{\omega} - i\pi\{\tilde{\omega}^3 - 2\tilde{\omega}^{-1}(\ln 2\tilde{\omega} + \tfrac{1}{2})\}. \quad . \quad . \quad . \quad . \quad (6.14)$$

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† Apparently the case for which the superconductor is described by the equations of F. and H. London over the whole temperature region at $\omega = 0$ is much rarer, and we shall not consider it.

‡ In our paper (Abrikosov *et al.* (1958)) there was an error in the derivation of this expression, and this also affected the equations which followed. The correct equation appears in the recently published work of Bardeen and Mattis (1958).

We also quote the expression for $Q(\omega)$ in the neighbourhood of $\tilde{\omega}=2$

$$Q(\tilde{\omega})=2\pi\left[1+\tfrac{1}{2}(1-\tfrac{1}{2}\tilde{\omega})\left(\ln\left|\frac{16}{2-\tilde{\omega}}\right|-1\right)\right]-i\pi^2\theta(\omega^2-2)(\tfrac{1}{2}\tilde{\omega}-1). \quad (6.15)$$

At $T=0$ the imaginary part of $Q(\tilde{\omega})$ is non-zero only for $\tilde{\omega}>2$. This is quite understandable from physical considerations as the imaginary part of the current determines the absorption, and in the absence of excitations this absorption can take place only by the break-up of pairs. The quantity 2Δ, taking into account the statistics, defines the amount of energy necessary for this.

For $T\neq 0$ the integrals depend considerably on the relation between Δ, ω and T. It should be noted that the condition $\Delta \ll T$ is only satisfied in the immediate neighbourhood of the critical temperature (for example $\Delta/T<0{\cdot}1$ only for $1-T/T_c<0{\cdot}001$), and thus does not correspond to a useful temperature interval. Therefore we only consider the cases $\Delta \gg T$ and $\Delta \sim T$.

(*a*) The case $T\sim\omega\ll\Delta$

The imaginary part of $Q(\omega)$ is exponentially small, as also is the change in the real part with temperature. Transforming the integrals we find

$$\begin{aligned}Q(\omega,T)&=\pi^2[1-(\omega/4\Delta)^2-2\exp(-\omega/2T)I_0(\omega/2\pi)\exp(-\Delta/T)]\\&\quad-4\pi i\sinh(\omega/2T)K_0(\omega/2T)\exp(-\Delta/T)\quad .\ .\ .\ .\ .\ (6.16)\end{aligned}$$

where K_0 and I_0 are Bessel functions of imaginary argument. In particular for $T\ll\omega\ll\Delta$ we have

$$\begin{aligned}Q(\omega,T)&=\pi^2[1-(\omega/4\Delta)^2-2(T/\pi\omega)-\exp(-\Delta/T)]\\&\quad-2i\pi\surd(\pi T/\omega)\exp(-\Delta T),\quad .\ .\ .\ .\ .\ .\ .\ .\ (6.17)\end{aligned}$$

and for $\omega\ll T\ll\Delta$

$$\begin{aligned}Q(\omega,T)&=\pi^2[1-(\omega/4\Delta)^2-2\exp(-\Delta/T)]-2i\pi(\omega/T)\\&\quad\times\ln(4T/\gamma\omega)\exp(-\Delta/T),\quad .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ (6.18)\end{aligned}$$

where $\gamma=1{\cdot}78$.

(*b*) *The case* $\omega\ll T\sim\Delta$

After a series of transformations we find

$$\begin{aligned}Q(\omega,T)&=\pi^2\tanh\frac{\Delta}{2T}\left\{1-\left(\frac{\omega}{4\Delta}\right)^2\right\}-i\pi\left[\frac{\omega}{T}\cosh^{-2}\frac{\Delta}{T}\ln 2\sqrt{\frac{2\Delta}{\omega}}\right.\\&\quad\left.+\frac{\omega}{\Delta}\left(1-\tanh\frac{\Delta}{2T}\right)-2\frac{\omega}{T}P\left(\frac{\Delta}{T}\right)\right]\quad .\ .\ .\ .\ .\ .\ .\ (6.19)\end{aligned}$$

where the function $P(x)$ is the integral

$$P(x)=\int_1^\infty\frac{d\epsilon}{\epsilon^2-1}\,\frac{\cosh x\epsilon-\cosh x}{(\cosh x\epsilon+1)(\cosh x+1)}\quad .\ .\ .\ .\ (6.20)$$

whose limiting values are

$$\left.\begin{aligned}&\text{for } x\gg 1: &\quad P(x)&=\exp(-x)\ln 2\gamma x\\&\text{for } x\ll 1: &\quad P(x)&=\frac{7}{2\pi^2}\xi(3)x.\end{aligned}\right\}\quad .\ .\ .\ .\ .\ .\ (6.21)$$

From (6.19) we find that for $\omega \ll T \ll \Delta$ the result is the same as with (6.18): for $\omega \ll \Delta \ll T$:

$$Q(\omega, T) = \pi^2 \frac{\Delta}{2T} - i\pi \left[\frac{\omega}{\Delta} + \frac{\omega}{2T} \left(\ln \frac{8\Delta}{\omega} - 1 \right) \right]. \quad . \quad . \quad (6.22)$$

(*c*) The case $T \ll \omega \sim \Delta$

Here there are two possibilities. If $\omega < 2\Delta$ the imaginary part is exponentially small. The expression for $Q(\omega)$ is

$$Q(\omega, T) = 2\pi \left[E(\omega/2\Delta) - \sqrt{\left\{ \pi T \left(\frac{1}{\omega} - \frac{1}{2\Delta} \right) \exp(-\Delta/T) \right\}} \right]$$
$$- 2i\pi \left[\sqrt{\left\{ \pi T \left(\frac{1}{\omega} + \frac{1}{2\Delta} \right) \right\}} \exp(-\Delta/T) \right]. \quad . \quad . \quad . \quad (6.23)$$

In particular, we obtain (6.17) for $T \ll \omega \ll \Delta$. If $\omega > 2\Delta$, a non-exponential term appears in the imaginary part

$$Q(\omega, T) = Q(\omega, 0) + 2\pi \exp[-(\omega - \Delta)/T] \sqrt{\left\{ \pi T \left(\frac{1}{2\Delta} - \frac{1}{\omega} \right) \right\}}$$
$$- 2\pi i \exp(-\Delta/T) \sqrt{(\pi T)} \left[\sqrt{\left(\frac{1}{\omega} - \frac{1}{2\Delta} \right)} - \sqrt{\left(\frac{1}{2\Delta} - \frac{1}{\omega} \right)} \right]. \quad (6.24)$$

In particular, for $T \ll \Delta \ll \omega$ we have

$$Q(\omega, T) = Q(\omega, 0) - 2\pi i \sqrt{(2\pi T \Delta)} \exp(-\Delta/T)/\omega. \quad . \quad . \quad (6.25)$$

(*d*) The case $T \sim \Delta \ll \omega$

The expression for $Q(\omega, T)$ becomes

$$Q(\omega, T) = Q(\omega, 0) - \frac{4\pi i \Delta}{\omega} \int_0^\infty \frac{d\phi}{\exp\{(\Delta \cosh \phi)/T\} + 1}. \quad . \quad (6.26)$$

Here $Q(\omega, 0)$ denotes the asymptotic value for $\omega \gg \Delta$, (6.14). For $T \ll \Delta \ll \omega$ we again obtain (6.25), but for $\Delta \ll T \ll \omega$ we find

$$Q(\omega, T) = Q(\omega, 0) - (2\pi i \Delta \omega) \ln(\pi T/\gamma\Delta). \quad . \quad . \quad . \quad (6.27)$$

We note that for all cases in which $\omega \gg \Delta$, the real part of Q is small compared to the imaginary part, which is $-\pi\omega/\Delta$ independently of the value of T. Thus for $\omega \gg \Delta$ the relation between current and the vector potential is:

$$\mathbf{j}(\mathbf{q}, \omega) = (3\pi i e^2 N \omega / 4mcvq) \mathbf{A}(\mathbf{q}, \omega). \quad . \quad . \quad . \quad . \quad . \quad (6.28)$$

This relation does not contain Δ, and is identical with that obtained from the theory of the anomalous skin effect for a normal metal as is to be expected. However, in this case we cannot limit ourselves to the basic term, since to find the difference between the superconducting and the normal states we must also take into account higher order terms. This is the reason for the inclusion of a small additional term in the eqns. (6.25), (6.26), and (6.27).

6.2. *The London Region*

We now calculate the conditions for the appearance of the London region $vq \ll \Delta$, and, as already stated, we shall not consider the possible but apparently rarer case when under static conditions the superconductor is of the London type over the whole temperature region.

As has already been noted, the London region can only appear near T_c. On the other hand, however, near to T_c the energy level separation Δ becomes very small, and since for $\omega/\Delta \gg 1$ the metal differs little from the normal state, the London region cannot continue right up to T_c and is in any case limited at the upper end by the condition $\omega \ll \Delta$.

To find more accurately the position of the London region we first find a relation between the current and the vector potential for $\Delta \gg v_q$. We take into account the previously noted fact that over the whole interesting frequency range we may take $\omega \ll v_q$, and also that the London region arises only very near to T_c, i.e. we may take $\Delta \ll T$. The necessary equation then follows from (6.6), in which only the integral with the difference of the two tangents and the last term are important.

Thus we find

$$\mathbf{j}(\mathbf{q}, \omega) = -\frac{e^2 N \mathbf{A}_q(\omega)}{mc}\left\{\frac{7}{4\pi^2}\zeta(3)\frac{\Delta^2}{T^2} - \frac{3i\pi\omega}{4vq}\right\}. \quad . \quad . \quad (6.29)$$

If we limit ourselves to the real part of this relation, we get the London equation, and the expression in the curly bracket plays the rôle of the ratio of the number of superconducting electrons N_s to the total number of electrons N. The imaginary part corresponds to absorption. We note that this expression is obtained under the assumptions $\omega \ll \Delta \ll T$ and $\omega \ll vq$, but there can be an arbitrary relationship between vq, and Δ and between vq and T. This explains the fact that apart from a small correction form this expression coincides with the corresponding one for the Pippard case.

As a criterion for the transition between the Pippard and London regions we may take the equality of the coefficients of A in the expression for the current. For the Pippard case, taking $\omega \ll \Delta \ll T$, from (6.13), (6.15), (6.25) we find

$$\mathbf{j} = -\frac{e^2 N}{mc}\mathbf{A}_q(\omega)\left\{\frac{3\pi^2}{\delta}\frac{\Delta^2}{vqT_c} - \frac{3i\pi\omega}{4vq}\right\}. \quad . \quad . \quad . \quad . \quad (6.30)$$

We compare this formula with (6.29). If we assume that the imaginary parts of both formulae are small compared to the real, the criterion coincides with that for the static case, namely that the London region occurs for

$$vq \ll vq_0 = 3\pi^4 T_c/14\zeta(3) \simeq 18 T_c. \quad . \quad . \quad . \quad . \quad (6.31)$$

Taking $q \simeq 1/\delta$, where δ is the penetration depth, and using formula (6.29), and the London formula for the penetration depth $\delta_L = \sqrt{\{(mc^2)/4\pi N_s e^2\}}$, it can be shown that this corresponds to the condition

$$\Delta \ll 2\pi^{3/2}(mc^2/Ne^2v^3)^{1/2}T_c^2. \quad . \quad . \quad . \quad . \quad . \quad (6.32)$$

From this inequality it follows that, for example, for aluminium the London region begins at $T - T_c \sim 4 \times 10^{-4} T_c$ and for tin at $T - T_c \sim 10^{-1} T_c$.

As the temperature increases the real part of (6.29) becomes small compared to the imaginary. But since in this case the superconductor differs little from the normal metal, we necessarily get the Pippard situation (we note that the imaginary part of (6.29) refers to this case also). Thus we may consider that the London region is limited by the condition

$$vq \ll vq_1 = (3\pi\omega/4\alpha\Delta^2)\,T_c^{\,2}, \quad \alpha = (7/4\pi^2)\zeta(3) \simeq 0{\cdot}2, \quad . \quad . \quad . \qquad (6.33)$$

or, after substitution of the London penetration depth

$$\Delta \gg 3^{1/3}\,\pi^{1/6}\,(4\alpha)^{-1/2}\,(mc^2/Ne^2v^2)^{1/6}\,T_c\,\omega^{1/3}. \quad . \quad . \quad . \quad . \quad . \qquad (6.34)$$

Comparing formulae (6.30) and (6.31) we get the condition for the appearance of the London region

$$\omega \ll \omega_c = 9\pi^4/(8\alpha)^3\,(mc^2/Ne^2v^2)\,T_c^{\,3}. \quad . \quad . \quad . \quad . \quad . \qquad (6.35)$$

This condition may define completely different frequencies for different elements. For example, for aluminium this frequency corresponds to $2{\cdot}7 \times 10^{-2}\,T_c$ or approximately $3 \times 10^9\,\mathrm{sec}^{-1}$, while for tin it is $0{\cdot}5\,T_c$ or $2 \times 10^{11}\,\mathrm{sec}^{-1}$. Incidentally tin may be considered by convention to belong to the superconductors of the Pippard type, since even at $T = 0$, $vq \sim vq_0$.

In view of the fact that the most interesting frequency range is that near to $\Delta(0)$, and that for a Pippard metal this range is practically always beyond the limits of the region defined by the inequality (6.35), we will not in general consider the London region.

Here it should also be pointed out that besides the limit on the frequency, the applicability of the London equations in the form (6.30) is limited on the high-temperature side by the condition that the dimensions of a pair, which are of the order v/Δ, must be small compared to the mean free path. If this does not hold, the position changes radically. Since on the average the mean free path may be considered to be of order 10^{-3} cm, and $v/\Delta \sim 10^{-4}$ cm, the region of applicability of (6.30) is, in general, small. For $v/\Delta \gg l$ no electrodynamics has been constructed and we shall not examine this case.

In conclusion we note that, as can easily be seen for frequencies greater than ω_c, a direct estimate gives $vq \gg T_c$ over the whole temperature region, including the neighbourhood of T_c, where the penetration depth is a maximum. Such a relation between vq and T was important in an earlier derivation.

6.3. *The Impedance*

The relation between **j** and **A** can be substituted in Maxwell's equations and an expression for the dependence of the vector potential on the coordinates can then be obtained. In the Pippard case considered above the corresponding calculations do not differ from the static case. For the case of specular reflection of the electrons from the surface the vector potential must be considered as reflected symmetrically across the boundary.

Taking the external field at the boundary as $H(0)$ we get

$$A=\frac{2}{\pi}\int_0^\infty \frac{H(0)\cos kz\,dk}{k^2+(3\pi Ne^2\Delta/mc^2v)\,Q(\omega)/k}, \quad . \quad . \quad . \quad . \quad . \qquad (6.36)$$

where

$$\delta=\int H\,dz/H(0)=\frac{8}{3\pi\sqrt{3}}\sqrt[3]{\left(\frac{mc^2v}{3\pi eN\Delta}\right)}\,\mathscr{Re}\,[\{Q(\omega)\}^{-1/3}].$$

The impedance is defined as follows

$$Z=R+iX=E(0)\Big/\int j\,dz=4\pi E(0)/cH(0)$$

$$=\frac{16\pi i\omega}{3\sqrt{3}c^2}\sqrt[3]{\left(\frac{mc^2v}{3\pi Ne^2\Delta}\right)}\{Q(\omega)\}^{-1/3}. \quad . \quad . \quad . \quad . \qquad (6.37)$$

For complex $Q(\omega)$ the value of the root is determined as an analytic continuation of the real root for real $Q(\omega)$.

In the diffuse scattering case we must take $A(z)=0$ outside the metal. In accordance with the theory of Reuter and Sondheimer (1948) this gives

$$Z=-\frac{4\pi^2 i\omega}{c^2}\left\{\int_0^\infty dk\ln\left[1+\frac{3\pi^2e^2N\Delta}{mc^2vk^3}Q(\omega)\right]\right\}^{-1}. \quad . \quad . \qquad (6.38)$$

This expression differs from (6.37) only by the factor 8/9.

It is convenient to relate the magnitude of the impedance to the value R of the resistance in the normal state, which for specular reflection is

$$R_n=(8\omega^{2/3}/3\sqrt{3}c^3)(mc^2v\pi/3Ne^2)^{-1/3}, \quad . \quad . \quad . \quad . \quad . \qquad (6.39)$$

as can be shown by substituting $Q=-\pi i\omega/\Delta$ in (6.37). The ratio Z/R_n is the same for both diffuse scattering and specular reflection and is given by

$$Z(\omega)/R_n=-2i\sqrt[3]{\{\pi\omega/\Delta Q(\omega)\}}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6.40)$$

For $T=0$ the frequency dependence of the impedance is obtained from eqns. (6.12)–(6.15)

$$Z(\omega)/R_n=2\sqrt[3]{\frac{\pi\omega}{\Delta\,|\Delta(\omega)|}}\left\{\sin\left(\tfrac{1}{3}\tan^{-1}\frac{|\mathscr{Im}Q|}{\mathscr{Re}Q}\right)-i\cos\left(\tfrac{1}{3}\tan^{-1}\frac{\mathscr{Im}Q}{\mathscr{Re}Q}\right)\right\}. \quad . \quad . \quad . \quad . \qquad (6.41)$$

It is interesting to note that the penetration depth changes very little over the region $\omega=0$ to $\omega=2\Delta$, and that $\delta(2\Delta)/\delta(0)={}^3\sqrt{(\pi/2)}=1{\cdot}16$.

For non-zero temperatures we shall now analyse the temperature dependence of the impedance at various frequencies.

(*a*) $\omega\ll\Delta(0)$

At the lowest temperatures we have successively $T\ll\omega\ll\Delta$, then T becomes of order ω, and finally we reach $\omega\ll T\ll\Delta$. This transition is described by (6.16), (6.17), and (6.18). Substituting these into (6.40) and taking into account the fact that $Q(\omega)$ differs little from the value of $\mathscr{Re}\,Q(\omega)$ for $\omega=0$, $T=0$, we have:

$$\begin{aligned}Z(\omega)/R_n=2\sqrt[3]{(\omega/\pi\Delta)}\{&(4/3\pi)\sinh(\omega/2T)\,K_0(\omega/2T)\exp(-\Delta/T)\\&-i[1+\tfrac{1}{3}(\omega/4\Delta)^2+\tfrac{2}{3}I_0(\omega/2T)\exp(-\Delta/T-\omega/2T)]\}.\end{aligned} \qquad (6.42)$$

When the temperature is increased further we reach $\omega \ll \Delta \sim T$, which then becomes the small region $\omega \ll \Delta \ll T$. This transition is described by (6.19)–(6.22). While $\Delta/T \gg \omega/\Delta$, $Q(\omega)$ will differ little from its value at $T=0$, and thus we find

$$\begin{aligned} Z(\omega)/R_n = 2\sqrt[3]{}\{\omega/\pi\Delta \tanh(\Delta/2T)\}[(2/3\pi)\ln 2\sqrt{}(2\Delta/\omega)+(1/3\pi)(\omega/\Delta) \\ +\{\coth(\Delta/2T)-1\}-(2/3\pi)(\omega/T)P(\Delta/T)\coth(\Delta/2T) \\ -1\{1+\tfrac{1}{3}(\omega/4\Delta)^2\}], \quad \ldots \quad (6.43) \end{aligned}$$

In the immediate neighbourhood of the critical temperature Δ becomes small and we have $\omega \ll \Delta \ll T$, $\omega \sim \Delta \ll T$, and $\Delta \ll \omega \ll T$. But, as has already been pointed out, the consideration of these cases is of no interest since they are all contained in a very small region. Instead of this we can use the fact that although (6.22) is not valid for $\Delta \ll \omega \ll T$ it nevertheless gives the correct limiting value, corresponding to the normal metal. Thus this expression (but not, of course, (6.42)) can be considered as an interpolation formula in the region $\omega \gg \Delta$.

(*b*) $\omega \sim \Delta(0)$

At low temperature we have $T \ll \omega \sim \Delta$. In this region (6.23) is valid for $\omega \ll 2\Delta(0)$, while (6.24) and (6.25) are valid for $\omega > 2\Delta(0)$. In the first case $Q(\omega)$ will differ little from the value $\mathscr{Re}\, Q(\omega)$ for $T=0$, which is $2\pi E(\omega/2\Delta)$, and the expression for the impedance is:

$$\begin{aligned} \frac{Z(\omega)}{R_n} = 2\sqrt[3]{}\left\{\frac{\omega}{2\Delta E(\omega/2\Delta)}\right\}\left[\frac{1}{3E(\omega/2\Delta)}\sqrt{}\left\{\pi T\left(\frac{1}{\omega}+\frac{1}{2\Delta}\right)\right\}\exp(-\Delta/T) \right. \\ \left. -i\left\{1+\frac{1}{3E(\omega/2\Delta)}\sqrt{}\left(\pi T\left(\frac{1}{\omega}-\frac{1}{2\Delta}\right)\exp(-\Delta T)\right)\right\}\right]. \quad \ldots \quad (6.44) \end{aligned}$$

For $\omega > 2\Delta(0)$ both parts of $Q(\omega)$ are of comparable magnitude and it is simpler to use the general formula (6.41).

As the temperature is increased we pass through $\omega \sim \Delta \sim T$ and reach $\Delta \ll T \sim \omega$. Here we can use the fact that for $\omega \gg \Delta$ the limiting value of the impedance is independent of temperature and corresponds to that for the normal metal. Therefore the use of (5.24) for interpolation will not introduce any significant error.

(*c*) $\omega \gg \Delta(0)$

In this case only the relation between T and Δ changes, as ω is always large compared to them. Equations (6·26)–(6.28) are applicable here, and taking into account the fact that for this case the real part of $Q(\omega)$ is small compared to the imaginary part, we find

$$\begin{aligned} \frac{Z(\omega)}{R_n} = 1+\left(\frac{\Delta}{\omega}\right)^2\left\{\frac{2}{3}\ln\frac{2\omega}{\Delta(0)}+\frac{1}{3}-\frac{\pi}{\sqrt{3}}\right\} - i\sqrt{3}\left[1+\left(\frac{\Delta}{\omega}\right)^2 \right. \\ \left. \times\left(\frac{2}{3}\ln\frac{2\omega}{\Delta(0)}+\frac{1}{3}+\frac{\pi}{3\sqrt{3}}\right)\right]. \quad \ldots \quad (6.45) \end{aligned}$$

These equations enable us to compare the theory with the experimental data.

§ 7. THE THERMAL CONDUCTIVITY OF SUPERCONDUCTORS

In superconductors heat transfer may take place by electronic excitations and by phonons. At temperatures which are not too low the electronic excitations make the main contribution to the thermal conductivity. In this case there are several possible scattering mechanisms, of which the scattering of excitations by impurities will usually be the most important. The scattering of excitations by phonons will be important only for very pure metals and we shall calculate the thermal conductivity of a superconductor for the case in which impurity scattering predominates. We write the kinetic equation for the excitations

$$\frac{\partial \epsilon}{\partial k}\frac{\partial n}{\partial r}-\frac{\partial \epsilon}{\partial r}\frac{\partial n}{\partial k}=\zeta(n). \qquad (7.1)$$

Here $\zeta(n)$ is the collision integral for the scattering of excitations by impurities, and we first find the form of this integral. It contains the scattering probability of excitations by impurities and the Hamiltonian of the interaction between an electron and the impurity can be written in the form

$$H^{\text{part}}=\sum a^{+}(\mathbf{k})\,a(\mathbf{k}')\,V(\mathbf{k},\mathbf{k}'). \qquad (7.2)$$

In this expression we now transform from the particle operators to the excitation operators, by (3.3) the terms which describe the scattering of excitations will have the form:

$$H^{\text{ex}}=\sum \alpha^{+}(\mathbf{k})\,\alpha(\mathbf{k}')\,V(\mathbf{k},\mathbf{k}')\,(u_k^2-v_k^2). \qquad (7.3)$$

and by (4.5) the last term is

$$\xi_k/\epsilon_k. \qquad (7.4)$$

The probability of an elastic transition $\mathbf{k}\to\mathbf{k}'$ for the excitations is

$$w_{kk'}=2\pi\,|V(k,k')\,\xi_k/\epsilon_k\,|^2\rho(\epsilon_k). \qquad (7.5)$$

The density of states ρ is found by the integration of the energy δ-function with respect to $d\xi$: $\rho=\epsilon_k/|\xi_k|$. Thus the probability of the above transition is

$$w_{kk'}=2\pi\,|V(k,k')|^2\,|\xi_k|/\epsilon_k. \qquad (7.6)$$

For the normal state the ratio $|\xi_k|/\epsilon_k$ equals unity, since $|\xi_k|=\epsilon_k$. In the superconducting state this ratio is some function of k (or ξ). It is well known that in the normal state the scattering of electrons may be characterized by a time τ which is independent of temperature, and that we may write the collision integral in the form:

$$\zeta(n)\to-(n-n_0)/\tau. \qquad (7.7)$$

In the superconducting state we must also take into account the factor $|\xi|/\epsilon$ by (7.6), i.e. instead of τ in (7.7) we must write τ' which differs from τ

by this factor†. Therefore in future we will write the right-hand side of (7.1) in the form

$$\zeta(n) = -(n-n_0)\,|\xi_k|/\tau\epsilon_k, \qquad (7.8)$$

where τ is the time constant which appears in the classical theory of electrical conductivity. Thus we write the kinetic equation (7.1) in the form

$$\frac{\partial\epsilon}{\partial\mathbf{k}}\frac{\partial n}{\partial\mathbf{r}} - \frac{\partial\epsilon}{\partial\mathbf{r}}\frac{\partial n}{\partial\mathbf{k}} = -\frac{(n-n_0)}{\tau}\frac{|\xi|}{\epsilon}. \qquad (7.9)$$

In non-superconducting metals an electric field is set up in the presence of a temperature gradient such that the resultant electric current is zero. However, for a superconductor there are two opposite flows of current—the superconducting and the normal, which are equal and opposite. The presence of a superconducting current with velocity $\mathbf{u}$ may be taken into account by substitution in (7.1)

$$\epsilon \to \epsilon + \mathbf{ku}.$$

We will bear this substitution in mind in further calculations, and we now turn to the solution of (7.1).

We substitute on the left-hand side the equilibrium function

$$n_0 = 1/(\exp(\epsilon/T)+1). \qquad (7.10)$$

On simplification we get

$$\frac{\partial\epsilon}{\partial k}\frac{\partial n_0}{\partial\epsilon}\frac{\epsilon\Delta T}{T} = \frac{(n-n_0)|\xi|}{\tau\epsilon}. \qquad (7.11)$$

It is interesting that the derivative $\nabla\epsilon$ cancels in the equation, and that in the result there are no terms connected with the differentiation of the energy level separation $\Delta(T)$. The energy flux equals

$$Q = \int \epsilon(\partial\epsilon/\partial k)\,n\,d\tau_k. \qquad (7.12)$$

Since the equilibrium function n_0 depends only on ϵ, the integral (7.12) vanishes for $n = n_0$ and the flux Q is completely determined by the difference $n - n_0$, which is given by (7.11). Substituting for $n - n_0$ from this equation we get

$$Q = \frac{\nabla T\,.\,\tau}{3T^2}\int \epsilon^2\left(\frac{\partial\epsilon}{\partial\xi}\right)^2\frac{\epsilon}{|\xi|}\,n'_0\,d\tau_k. \qquad (7.13)$$

---

† The replacement of τ by τ' is carried out, as can easily be seen, by multiplication by the ratio of the velocity of excitations to the velocity of electrons v at the Fermi surface.

$$\partial\epsilon/\partial\xi_n = \xi_n/\epsilon.$$

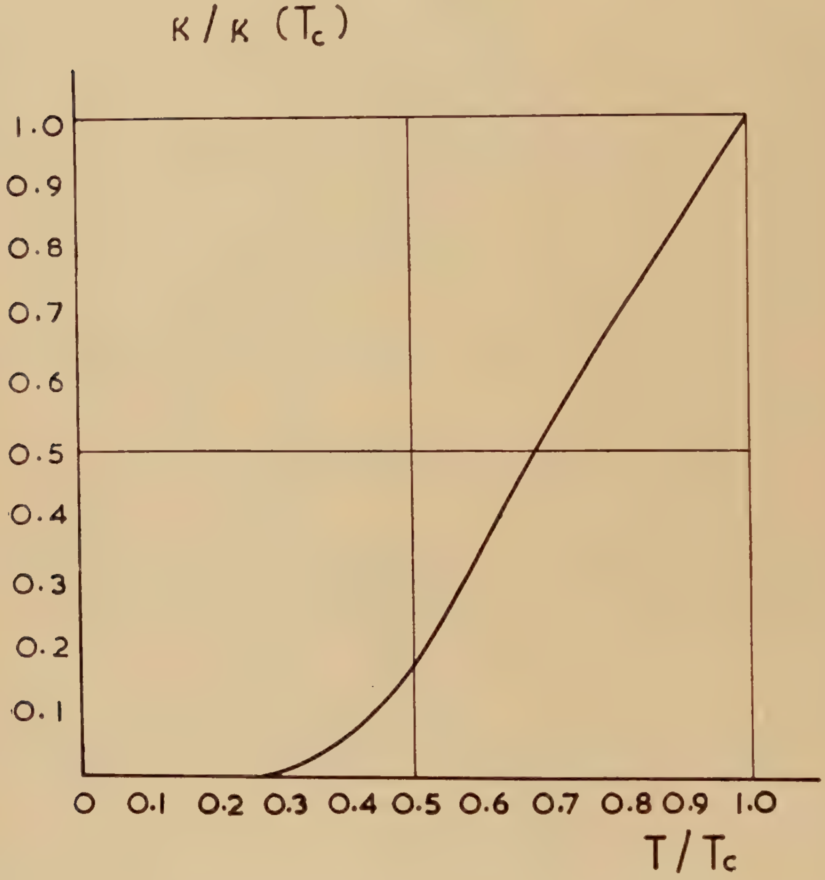
Consequently we have the relation $\tau v = \tau'\xi k/\epsilon$, which shows that the mean free paths for electrons in the normal state and for excitations in the superconducting state are equal.

We thus find the magnitude of the coefficient of thermal conductivity to be

$$\kappa = \frac{\tau}{3T^2}\int \epsilon^2 \left(\frac{\partial \epsilon}{\partial \xi}\right) \frac{1}{\exp(\epsilon/T)+1}\,\frac{1}{\exp(-\epsilon/T)+1}\,d\tau. \quad . \quad . \quad (7.14)$$

If we introduce a new variable of integration $\xi = \cosh\phi\Delta$, then formula (6.14) reduces to a form which is convenient for the calculation of the temperature dependence.

Fig. 5



$$\kappa = \frac{2\tau}{3T^2}\nu\Delta^3 \int_0^\infty \cosh^2\phi \sinh\phi \, d\phi \, \frac{1}{\exp(\Delta\cosh\phi/T)+1}. \quad . \quad (7.15)$$

Equation (7.15) gives the electronic part of the coefficient of thermal conductivity of a superconductor when the electrons are scattered mainly at impurities. We note that at the transition point ($\Delta \to 0$) (7.15) gives a value of κ which corresponds to that for the normal metal obtained from the usual theory of the electrical conductivity of metals. It can also be rewritten in the following form which is convenient for comparison with experiment

$$\frac{\kappa(T)}{\kappa(T_c)} = \frac{12}{\pi^2}\frac{T}{T_c}\int_{\Delta/2\tau}^{\infty}\frac{x^2\,dx}{\cosh^2 x}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7.16)$$

Zavaritskii (1958) compared the temperature dependence of κ given by (7.16) (see fig. 5) with the experimental data for Al and Zn and obtained good agreement. The data for zinc deviate from (7.16) only below 0·2°K, when the lattice conductivity becomes important.

§ 8. CONCLUSION

Thus, one of the most enigmatic of natural phenomena—superconductivity—has at last been explained. The agreement of the theory of Bardeen, Cooper and Schrieffer with experiment has proved even better than could have been expected from a theory which is based on the model of a Hamiltonian with a four-fermion interaction. At the same time, although the phenomenon of superconductivity can be considered to have been completely explained, there still remain isolated questions which need to be investigated on the basis of this theory. The behaviour of superconductors in high magnetic fields (near to H_i) has not yet been investigated. In connection with this it is apparently necessary to develop a gauge-invariant method independent of perturbation theory and the work of Gor'kov (1958), in which he has applied the gauge-invariant technique of quantum field theory to the theory of superconductivity deserves attention and has considerable methodological interest.

There is also the question of the possibility of the existence of Bose type excitations in superconductors (Bogolyubov *et al.* 1958). The Fermi excitations considered above had a characteristic spectrum with an energy gap. The presence of, for example, sound vibrations in the form of phonons (with an energy spectrum without a gap) would not interfere with the existence of superconductivity just as phonons do not prevent superfluidity. However, if there were such a branch in the spectrum, this would considerably affect the temperature dependence of all the thermodynamic variables. The question of Bose oscillations of the system of Fermi-particles considered has however no great importance in the theory of superconductivity. This is because such oscillations would be related to oscillations of the electrical charge density, which, owing to the large Coulomb interaction would be in the optical frequency range, so that to excite them, energies of the order of an electron volt would be needed. Thus the whole question of a Bose branch in the spectrum of Fermi particles is only of academic interest.

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